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THE CHEMICAL SOCIETY.

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I.—*Mandeliminohydrin.**

By John Edwin Mackenzie.

The amides of monobasic organic acids are generally represented as having the constitution $R{\cdot}CO{\cdot}NH_2$. To the isomeric formula, $R{\cdot}C(OH){:}NH$, the name iminohydrin has been applied and a large

* Note by James Walker.—The circumstance that the iminohydrins are good conductors of electricity and are at the same time practically neutral in aqueous solution renders these substances of great interest from the point of view of the theory of amphoteric electrolytes (*Proc. Roy. Soc.*, 1904, **73**, 155; **74**, 271). Some years ago I accordingly prepared glycolliminohydrin and lactiminohydrin in a state of purity and investigated some of their physico-chemical properties. From measurements of the degree of hydrolysis of glycolliminohydrin hydrochloride by the methods of methyl acetate catalysis and of electromotive force, it appeared that in $N/8$-solution the salt was hydrolysed to the extent of about 50 per cent. The degree of hydrolysis of the sodium salt of glycolliminohydrin, judged from its electrical conductivity, was at the same concentration also about 50 per cent. The results with lactiminohydrin were similar. From these determinations it was possible to calculate the molecular conductivity of the iminohydrins themselves by means of the theory of amphoteric electrolytes. The calculated value indicated that the iminohydrins should be very feeble conductors of electricity, and bore no sort of relationship to the conductivity actually observed, which is high and roughly that of a salt.

The natural conclusion to draw was that the iminohydrins are not in reality amphoteric electrolytes, and that the formula usually attributed to them is erroneous. However, as the two examples investigated were of a very similar nature, it seemed desirable to study other members of the class, and at my request Dr. J. E. Mackenzie began their preparation. Other duties, however, compelled him to relinquish the work, which was then taken up by Dr. H. G. Rule, and carried to a successful conclusion, the true nature of the iminohydrins being disclosed.

number of derivatives of iminohydrins, such as the iminoalkyl ethers, $R{\cdot}C(OAlk){:}NH$, and their hydrochlorides,

$$R{\cdot}C(OAlk){:}NH,HCl,$$

have been described by Pinner and his collaborators (Pinner, "Die Iminoäther," etc.).

Free iminohydrins are stated by Eschweiler (*Ber.*, 1897, **30**, 998) to be formed by the action of water on an imino-ether, thus, $R{\cdot}C(OAlk){:}NH + H_2O = R{\cdot}C(OH){:}NH + Alk{\cdot}OH$, or of a suitable base on the imino-ether hydrochloride. It is a curious point that Eschweiler describes only three substances, namely, glycolliminohydrin, $CH_2(OH){\cdot}C(OH){:}NH$; lactiminohydrin,

$$CH_3{\cdot}CH(OH){\cdot}C(OH){:}NH;$$

and α-hydroxy*iso*butyriminohydrin, $(CH_3)_2CH(OH){\cdot}C(OH){:}NH$, all of which are derivatives of α-hydroxy-acids. In 1911 Professor James Walker suggested to me the preparation of those and other iminohydrins in order that their physical properties might be determined with accuracy. I repeated the preparation of the two latter substances, and also obtained the so-called mandeliminohydrin. It was formed from the corresponding ethyl ether hydrochloride and freshly precipitated silver hydroxide according to the equation

$$C_6H_5{\cdot}CH(OH){\cdot}C(OEt){:}NH,HCl + AgOH = C_6H_5{\cdot}CH(OH){\cdot}C(OH){:}NH + EtOH + AgCl.$$

As will be shown in the succeeding paper by Dr. H. G. Rule, the constitution of this substance may be interpreted in a totally different manner and therewith that of Eschweiler's so-called iminohydrins.

"Mandeliminohydrin," when pure, is, like Eschweiler's iminohydrins, a fairly stable substance.

My attempts to prepare acetimino-, benzimino-, and one or two other imino-hydrins were unsuccessful.

Experimental.

"*Mandeliminohydrin*," $C_6H_5{\cdot}CH(OH){\cdot}C(OH){:}NH$.

The ethyl ether hydrochloride was prepared by mixing 13·3 grams of benzaldehydecyanohydrin, 5·6 grams of ethyl alcohol, and 41·3 grams of ether in a flask provided with inlet tube and exit calcium chloride tube. The flask was immersed in ice, and dry hydrogen chloride was passed in until an increase in weight of 5 grams had taken place. The mixture was allowed to remain for two days and then filtered, the residue being washed with ether (dried over sodium), and placed in a vacuum desiccator over potassium hydroxide. (Found, Cl = 16·3. Calc., Cl = 16·4 per

cent.) The crystalline product weighed 19·5 grams, the theoretical yield being 21·5 grams.

A solution of 17 grams of silver nitrate in water was precipitated by the addition of insufficient sodium hydroxide, and the precipitate rapidly washed. It was then suspended in 60 c.c. of water, and 19 grams of the crystalline ethyl ether hydrochloride were slowly added, and the two mixed with a pestle. The mixture, which was contained in a glass basin surrounded by ice and salt, assumed the consistency of porridge, so an addition of 40 c.c. of water was made. On filtering some of the mixture, the filtrate was still found to contain much chlorine. The mixture was therefore allowed to remain overnight in the ice-chest, and filtered next morning. To the filtrate, hydrogen sulphide was added in order to precipitate any unchanged silver hydroxide in solution. The clear filtrate from the silver sulphide was evaporated at about 40° in a strong draught until of a syrupy consistency. The residual yellow syrup was triturated with ether, which removed the colouring matter and left a colourless solid. On cooling a hot alcoholic solution of the solid, there separated colourless crystals, which darkened in colour at about 160° and melted and decomposed between 173° and 179°:

0·1090 gave 0·2540 CO_2 and 0·0585 H_2O. C = 63·55; H = 5·96.
0·1789 ,, 14·2 c.c. N_2 (moist) at 16° and 764 mm. N = 9·37.
$C_8H_9O_2N$ requires C = 63·58; H = 5·96; N = 9·27 per cent.

"Mandeliminohydrin" is moderately soluble in cold, but very readily so in hot methyl and ethyl alcohols. It is sparingly soluble in ether, benzene, or light petroleum. When pure, it is fairly stable. The yield of pure substance was very small, being less than 1 gram.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH. [*Received, July 2nd*, 1917.]

II.—*Amidine Salts and the Constitution of the so-called Iminohydrins.*

By HAROLD GORDON RULE.

THE iminohydrins, or *iso*amides, are first mentioned by Eschweiler (*Ber.*, 1897, **30**, 1003), who prepared them from the corresponding imino-ether hydrochlorides by the action of moist silver oxide or by the interaction of the free imino-ethers and water. The result-

ing compounds, from their analysis and apparent unimolecular condition in aqueous solution, were represented as having the constitution R·C(OH):NH, isomeric with the acid amides.

Thus the formation of glycolliminohydrin, the first of these compounds to be obtained from the corresponding ethyl ether hydrochloride, was explained according to the equation

$$OH\cdot CH_2\cdot C(OEt){:}NH,HCl + AgOH = OH\cdot CH_2\cdot C(OH){:}NH + AgCl + EtOH,$$

the iminohydrin, together with a large proportion of glycollamide, being supposed to result from the direct hydrolytic action of the water present. In addition to the above, lactiminohydrin and α-hydroxy*iso*butyriminohydrin were prepared and very shortly described.

The chief characteristics of these compounds, as noted by Eschweiler, are their high melting points, fusion being generally accompanied by decomposition, the liberation of ammonia by alkalis, and their peculiar reaction towards certain metallic salts, the glycollic compound, for example, slowly giving a deposit of calcium glycollate on the addition of a solution of calcium chloride. The latter action was supposed to take the course

$$2OH\cdot CH_2\cdot C(OH){:}NH + CaCl_2 + 2H_2O = (OH\cdot CH_2\cdot CO_2)Ca + 2NH_4Cl.$$

Eschweiler further states that the iminohydrins are basic in character, and claims to have isolated definite hydrochlorides of the general type R·C(OH):NH,HCl, which are neutral in aqueous solution.

The failure of all attempts to effect an interconversion between the iminohydrins and their apparent isomerides, the acid amides, led to an extended investigation by Hantzsch (*Ber.*, 1901, **34**, 3142), who showed that these compounds were comparatively strong electrolytes, having in reality a molecular weight double that assigned to them by Eschweiler. In opposition to the latter author, Hantzsch finds the iminohydrin hydrochloride to be strongly hydrolysed in aqueous solution, and also comments on the fact that all the known iminohydrins are derivatives of α-hydroxy-acids.* In spite of numerous attempts, however, he was unable to prepare other types. In explanation of the discovery that the iminohydrins were electrolytes of the general formula $(R\cdot CO\cdot NH_2)_2$, they were represented as having the constitution $NH{:}CR\cdot O\cdot NH_2{:}CR\cdot OH$, the complex being supposed to ionise in aqueous solution into the ions $(NH{:}CR\cdot O)'$ and

* In a patent application Eschweiler makes the bare claim to have prepared acet- and benz-iminohydrins, but no further details are given.

$(NH_2{:}CR{\cdot}OH)$'. The failure to establish any relationship to the acid amides, despite the similarity between the structure of these compounds and that suggested above for the iminohydrins, was met by Hantzsch with the statement that "amides and *iso*amides (iminohydrins) are not isomerides, but polymerides, and their relations are therefore different from those of genuine tautomerides, which possess equal molecular weights." The hydrochloride of glycolliminohydrin was nevertheless formulated as

$$OH{\cdot}CH_2{\cdot}C(OH){:}NH_2Cl,$$

in which case we should have a true isomeride of glycollamide existing in combination with hydrochloric acid.

More recently, the behaviour in solution of glycolliminohydrin, lactiminohydrin, and their salts has been examined by Professor James Walker (see Note to preceding paper), with results which led him to the conclusion that these compounds are not true amphoteric electrolytes, and that the formula assigned to them by Hantzsch is incorrect. For this reason, and since all previous attempts to prepare iminohydrins other than α-hydroxy-derivatives had failed, pointing to the possibility that the hydroxyl group was an integral part of the molecule, the following investigation was undertaken.

Several representatives of this class have been prepared and examined, and all were found to possess the high molecular weight and saline properties characteristic of glycolliminohydrin. The early preparation of the methoxyacetic and the phenylacetic derivatives showed that the formation of an iminohydrin was in no way dependent on the presence of an α-hydroxy-group in the molecule of the interacting imino-ether. Subsequently, an examination of the comparatively stable mandelic compound * led to the discovery that the iminohydrins are complex amidine salts of the general formula $R{\cdot}C(NH_2){:}NH,R{\cdot}CO_2H$. This was confirmed by the synthesis of mandeliminohydrin (mandelamidine mandelate) from mandelamidine hydrochloride and sodium mandelate,

$$C_6H_5{\cdot}CH(OH){\cdot}C(NH_2){:}NH,HCl + C_6H_5{\cdot}CH(OH){\cdot}CO_2Na = C_6H_5{\cdot}CH(OH){\cdot}C(NH_2){:}NH,C_6H_5{\cdot}CH(OH){\cdot}CO_2H + NaCl,$$

and of Eschweiler's original glycolliminohydrin (glycollamidine glycollate) from the corresponding amidine hydrochloride and sodium glycollate,

$$OH{\cdot}CH_2{\cdot}C(NH_2){:}NH,HCl + OH{\cdot}CH_2{\cdot}CO_2Na = OH{\cdot}CH_2{\cdot}C(NH_2){:}NH,OH{\cdot}CH_2{\cdot}CO_2H + NaCl.$$

In connexion with the latter synthesis, for which glycollamidine

* See preceding paper by J. E. Mackenzie.

hydrochloride had first to be prepared, some of Eschweiler's work on the iminohydrin (amidine) salts has been repeated and several inaccuracies have been corrected.

From the above point of view, a review of the properties of the "iminohydrins" presents no peculiarities. Evidence of saline character is furnished by high melting points, insolubility in ether or hydrocarbons, and by high electrical conductivities in aqueous solution, the latter in the case of the glycollic compound being very little short of the value for a typical salt such as sodium acetate. The reaction with metallic salts is seen to be an example of ordinary double decomposition, that between glycolliminohydrin and calcium chloride following the course

$$2OH\cdot CH_2\cdot C(NH_2){:}NH,OH\cdot CH_2\cdot CO_2H + CaCl_2 = 2OH\cdot CH_2\cdot C(NH_2){:}NH,HCl + (OH\cdot CH_2\cdot CO_2)_2Ca.$$

The soluble substance left in solution is glycollamidine hydrochloride, and not ammonium chloride, as assumed by Eschweiler, and later by Hantzsch. Characteristic of amidine salts is the disruption which accompanies fusion and the readiness with which ammonia is evolved on treatment with alkalis, whilst the decomposition suffered by the iminohydrins in general on heating with aqueous solvents is due to hydrolysis of the amidine into amide and ammonia. This is well illustrated in the case of the phenylacetic compound, where attempted crystallisation from alcohol was found to lead to the production of phenylacetamide and ammonium phenylacetate,

$$CH_2Ph\cdot C(NH_2){:}NH,CH_2Ph\cdot CO_2H + H_2O = CH_2Ph\cdot CO\cdot NH_2 + CH_2Ph\cdot CO_2NH_4.$$

The contradictory statements of Eschweiler and Hantzsch in connexion with the neutrality of the "iminohydrin salts" are also made clear, since these authors believed that the iminohydrin, $(R\cdot C(OH){:}NH)_2$, was capable of uniting with two molecules of hydrochloric acid to yield two molecules of the salt,

$$R\cdot C(OH){:}NH,HCl.$$

The hydrochloride, in reality an amidine salt, as isolated by Eschweiler, proved to be neutral when dissolved in water, whilst hydrolysis measurements carried out by Hantzsch with a solution containing one molecular proportion of iminohydrin to two of hydrochloric acid naturally led to the conclusion that the salt was considerably hydrolysed. The organic acid which is liberated in the latter case remains practically non-ionised in the presence of the excess of hydrochloric acid, thus accounting for the apparent dissociation values of 50 per cent. obtained by Walker (see Note to preceding paper) for glycolliminohydrin and lactiminohydrin

hydrochlorides, and by the author for the methoxyacetic and mandelic derivatives.

Mechanism of the Interaction of Imino-ethers and Water.

Pinner, in his monograph on the imino-ethers ("Die Imidoäther und ihre Derivate"), states that these compounds decompose slowly on keeping, generally giving rise to the alcohol and nitrile from which they are derived. In some cases the nitrile may polymerise on being liberated, whilst in others the decomposition may take place in a different manner and lead to the formation of an acid amide. An example of the latter type is furnished by α-hydroxy*iso*butyrimino-ethyl ether (Pinner, *loc. cit.*, p. 37), which on attempted distillation decomposes into the corresponding amide and alcohol, and it is probable that the interaction between benzimino-ethyl ether and water to form cyaphenin (Mackenzie, P., 1913, **29**, 175) is due to the initial formation and subsequent polymerisation of benzonitrile.

In those reactions where water is present, however, other changes may take place. Imino-ethers are at once strongly alkaline and readily hydrolysable compounds, and the work of Pinner has shown that the imino- and alkyloxy-groupings are extremely sensitive to attack, the actual group or groups affected depending on the reagent employed. In particular, ammonia reacts with imino-ether hydrochlorides with great readiness to form amidine salts. Although in no single instance was any trace of free ammonia observed during the above interactions between imino-ether and water, it was found by experiment that the addition of an equivalent of ammonium mandelate to an aqueous suspension of mandelimino-ethyl ether not only doubled the yield of amidine mandelate, but the deposition of the salt commenced almost immediately after the addition had been made. It seems probable, then, that in the interaction of imino-ethers and water, the first step is autohydrolysis of a portion of the substance in the alkaline medium to form the ammonium salt of the corresponding acid,

$$R\cdot C(OEt){:}NH + 2H_2O = R\cdot C(ONH_4){:}O + EtOH.$$

This salt, then, reacts with more free imino-ether to give the amidine salt or iminohydrin,

$$R\cdot C(ONH_4){:}O + R\cdot C(OEt){:}NH = R\cdot C(NH_2){:}NH,R\cdot CO_2H + EtOH.$$

In this connexion, Pinner, in describing the formation of amidine hydrochloride from imino-ether hydrochloride and a slight excess of alcoholic ammonia, remarks on the precipitation of

ammonium chloride, which then slowly dissolves with the formation of the soluble amidine salt.*

The production of amide is probably caused by direct hydrolysis of imino-ether and amidine in the alkaline solution, and the amount formed in any given experiment does not appear to bear any constant relation to that of the amidine salt.

Experimental.

The method of preparation adopted by Eschweiler, and later by Hantzsch, in which the imino-ether hydrochloride is added in small portions at a time to an equivalent amount of silver oxide suspended in water, led to such small and variable yields that its use was abandoned. Yields of 30—35 per cent. were obtained by allowing the free imino-ethers to remain with excess of water for some days at the ordinary temperature. During this time, the originally strong alkaline reaction of the imino-ether gradually disappeared, and a mixture of iminohydrin and acid was produced. At first the iminohydrin was isolated by repeated crystallisation from a suitable solvent. In some later cases, the dried products of reaction were extracted with ether in a Soxhlet apparatus, the insoluble iminohydrin being left behind in a comparatively pure state.

"Glycolliminohydrin" (glycollamidine glycollate) was prepared in a 30 per cent. yield by dissolving glycollimino-ethyl ether in excess of water and allowing the solution to remain for ten or twelve days. On evaporation to dryness in a vacuum over sulphuric acid, and repeated recrystallisation of the residual solid from alcohol, the pure iminohydrin was obtained in well-defined plates melting and decomposing at 166—168°. Eschweiler (*loc. cit.*) gives 161—162°.

In the hope of isolating some definite oxidation or reduction product, an electrolysis of the iminohydrin in aqueous solution was carried out in a divided cell. An analysis of the electrode gases, however, indicated complete disruption of the iminohydrin molecule. Similarly, all attempts by chemical means to isolate a basic or acidic component other than ammonia or glycollic acid, both of which were believed to be products of hydrolysis, led to no result.

Earlier attempts to prepare acet- and benz-iminohydrins were also unsuccessful (compare Hantzsch, *loc. cit.*, and Mackenzie, P., 1913, **29**, 175), the only recognisable products of reaction in the

* Since the above was written, a paper has been published by A. Knorr (*Ber.*, 1917, **50**, 229), in which the author claims to have shown conclusively that free ammonia does not react with free imino-ethers, but that amidine hydrochlorides are formed from them by reaction with ammonium chloride.

case of benzimino-ethyl ether being benzamide, cyaphenin, and a little ethyl benzoate. The first indication that the presence of an α-hydroxy-group was not an essential condition for the formation of an iminohydrin was given by the preparation of methoxyacetiminohydrin.

Methoxyacetimino-ethyl Ether, $CH_3 \cdot O \cdot CH_2 \cdot C(O \cdot C_2H_5) : NH$.

Methoxyacetonitrile (29 grams), prepared from paraformaldehyde according to Wedekind's method (*Ber.*, 1903, **36**, 1383), was dissolved in ether and treated with an equivalent (24 c.c.) of absolute alcohol. The solution was cooled in ice, and dry hydrogen chloride (15 grams) passed in. After a short time, the liquid separated into two layers, and subsequently methoxyacetimino-ethyl ether hydrochloride crystallised out.

Some of the hydrochloride (16 grams) was shaken with ether and a concentrated solution of potassium carbonate. Much carbon dioxide was evolved, and the ethereal extract, after drying over sodium sulphate, was distilled. The boiling point of the distillate slowly rose to 136°, where it remained constant. The yield of methoxyacetimino-ethyl ether (b. p. 136°) was 5·5 grams.

The imino-ether is a colourless liquid with a peculiar odour; it is alkaline to litmus and miscible in all proportions with water. Ammonia is readily evolved on treatment with alkalis:

0·1789 gave 0·3381 CO_2 and 0·1474 H_2O. C = 51·52; H = 9·22.

$C_5H_{11}O_2N$ requires C = 51·25; H = 9·47 per cent.

It is probable that the substance was not quite pure, since all imino-ethers decompose to some extent on heating. An attempt to purify a portion by distillation under 50 mm. pressure gave a distillate passing over at 66—67°. This specimen on analysis proved to be no purer than the above.

"*Methoxyacetiminohydrin*" (*methoxyacetamidine methoxyacetate*) was obtained by allowing the free imino-ether (12 grams), mixed with excess of water, to remain at the ordinary temperature for five weeks. The water was removed in a vacuum over sulphuric acid, and the resulting mixture recrystallised repeatedly from alcohol containing about a third of its volume of benzene. The iminohydrin (2·2 grams) was obtained in large, well-shaped needles melting at 162—164°:

0·1835 gave 0·2715 CO_2 and 0·1332 H_2O. C = 40·35; H = 8·06.

$C_6H_{14}O_4N_2$ requires C = 40·42; H = 7·93 per cent.

It is readily soluble in alcohol and moderately so in water. In ether or benzene it dissolves sparingly. On heating with aqueous sodium hydroxide, ammonia is evolved.

Molecular Weight in Aqueous Solution (Cryoscopic Method).

Using 20 grams of solvent, the following data were obtained (K = 1870):

0·1225 gave $\Delta t = -0·129°$. M.W. = 89.
0·2481 ,, $\Delta t = -0·250°$. M.W. = 93.
0·3067 ,, $\Delta t = -0·309°$. M.W. = 93.

$C_6H_{14}O_4N_2$ requires M.W. = 178, hence at the above dilutions the substance is almost completely ionised

Electrical Conductivity in Water at 25°.

The following determinations were made, using electrodes covered with a deposit of "grey" platinum, and to reduce still further errors arising from the oxidation at the electrodes, the electrolyte at each dilution was freshly prepared from a stock solution by the addition of the requisite amount of water ($\mu_{25} = 1·6 \times 10^{-6}$).

An $N/20$-solution was prepared by dissolving 0·8907 gram of the "iminohydrin" up to 100 c.c.

v	20	40	100	200	400	1000	2000
μ_{25}.....	60·9	64·0	67·8	69·8	70·8	71·6	72 0

At dilution $v = 2000$ oxidation was noticeable, as shown by the dropping of the cell-resistance. The figures show methoxyacetiminohydrin to be a good electrolyte, with a conductivity at high dilutions comparable with that of glycolliminohydrin, for which Hantzsch finds $\mu_{25} = 79·5$ at $v = 2048$.

Hydrolysis of "Methoxyacetiminohydrin Hydrochloride."

According to Eschweiler and Hantzsch, the iminohydrins form hydrochlorides of the general type R·C(OH):NH,HCl, salts which are considerably hydrolysed in aqueous solution. Walker (see Note to preceding paper) finds this hydrolysis in the case of the glycollic and lactic derivatives to approximate to 50 per cent. in $N/8$-solution.

The hydrolysis at the same dilution of methoxyacetiminohydrin hydrochloride was measured by the methyl acetate catalysis method, and found in this case also to be almost exactly 50 per cent.

Experiments directed towards the preparation of the unsubstituted "iminohydrins" corresponding with benzoic, phenylacetic, and acetic acids met at first with no success. As has been already stated, benzimino-ethyl ether reacts with water to give cyaphenin, and failure in the cases of phenylacet- and acet-imino-ethyl ethers was subsequently found to be due to hydrolysis of the "imino-

hydrins" during attempted purification by crystallisation. The two latter compounds were eventually obtained from the crude reaction mixture after removing the accompanying acid amide by extraction with ether in a Soxhlet apparatus.

"Acetiminohydrin" (*Acetamidine Acetate*),
$CH_3 \cdot C(NH_2) : NH, CH_3 \cdot CO_2H$.

Acetimino-ethyl ether hydrochloride, prepared from acetonitrile (37·5 grams), alcohol, and hydrogen chloride in the usual manner, was converted into the free imino-ether by shaking with ether and a concentrated solution of potassium carbonate. The bulk of the ether was cautiously removed on the water-bath, and the residual liquid mixed with excess of water in a stoppered bottle. After ten weeks, the still faintly alkaline solution was evaporated to dryness in a vacuum over sulphuric acid, and the solid residue extracted with ether in a Soxhlet apparatus. The residue, melting at 66—148°, was partly soluble in benzene, the solution depositing crystals of acetamide (m. p. 79—82°). The insoluble portion, amounting to 3 grams, melted at 155—175°. The latter was purified by solution in cold alcohol and precipitation with benzene, giving a final product melting and decomposing at 185—187°.

All attempts to recrystallise it from warm alcohol or ethyl acetate, with or without the addition of benzene, resulted in the decomposition of the iminohydrin.

Qualitative tests showed that this substance was a good electrolyte, whilst its high melting point, insolubility in ether, and the evolution of ammonia with sodium hydroxide, showed it to be of the same class of substances as glycolliminohydrin. Owing to the low yield and its unstable nature, it was not further examined.

"Phenylacetiminohydrin" (*Phenylacetamidine Phenylacetate*),
$C_6H_5 \cdot CH_2 \cdot C(NH_2) : NH, C_6H_5 \cdot CH_2 \cdot CO_2H$.

Free phenylacetimino-ethyl ether, prepared from phenylacetonitrile (Pinner, "Die Imidoäther," p. 66), was allowed to remain in contact with water at the ordinary temperature for several weeks. The semi-solid mass was filtered, and the solid portion, after drying, extracted with ether in a Soxhlet apparatus. After thirty hours' extraction, the iminohydrin was left behind in a pure state, melting and decomposing at 227—230°:

0·1586 gave 0·4138 CO_2 and 0·0974 H_2O. C = 71·13; H = 6·82.
$C_{16}H_{18}O_2N_2$ requires C = 71·10; H = 6·72 per cent.

By solution in ethyl acetate and precipitation with benzene, a product of the original melting point was obtained in very fine

needles. The substance is very sparingly soluble in water, soluble in alcohol, and insoluble in benzene or ether. With aqueous alkalis, ammonia is readily evolved, and the compound is of the same unstable nature as acetiminohydrin, attempted recrystallisation from alcohol or water leading to partial decomposition into amide and the ammonium salt of the corresponding acid. For this reason, it was not further examined.

The four "iminohydrins" described above, derivatives of glycollic, methoxyacetic, acetic, and phenylacetic acids, were not suited to a detailed investigation on account of their instability towards solvents and their general physical properties. A more convenient subject for examination was found in "mandeliminohydrin."

"*Mandeliminohydrin*" (*Mandelamidine Mandelate*),
$C_6H_5 \cdot CH(OH) \cdot C(NH_2) : NH, C_6H_5 \cdot CH(OH) \cdot CO_2H$.

This compound had already been obtained in small quantities by Mackenzie (see preceding paper) by the interaction of aqueous silver oxide and mandelimino-ethyl ether hydrochloride. In the preparation of larger quantities, it was obtained from benzaldehyde as follows.

Moist potassium cyanide (80 grams) was placed in a flask and covered with an ethereal solution of one equivalent (106 grams) of benzaldehyde. The whole was cooled in ice, and rather less than one equivalent (50 c.c.) of concentrated hydrochloric acid added slowly with constant shaking. The ethereal solution was decanted and dried for twenty-four hours over anhydrous sodium sulphate, after which it was poured off and cooled in ice. Equivalent amounts of alcohol (46 grams) and dry hydrogen chloride (36·5 grams) were added, and after a short time the liquid became almost solid, owing to the separation of mandelimino-ethyl ether hydrochloride. In a few hours the latter (135 grams) was collected.

The hydrochloride was suspended in ether and shaken with a concentrated solution of potassium carbonate. On removal of the ethereal layer and evaporation of the solvent in a vacuum, the free imino-ether (87 grams) remained as a white solid.

The imino-ether was introduced into a stoppered bottle containing excess of water, and the latter placed in a shaking machine. After five or six days, the bulk of the solid suddenly passed into solution, when the reaction mixture was removed and the water evaporated in a vacuum over sulphuric acid. The dry residue was transferred to a Soxhlet apparatus and extracted for some hours with ether, leaving an insoluble portion melting and decomposing at about 180° which, after one crystallisation from alcohol,

gave the pure iminohydrin (25 grams), melting and decomposing at 185—187°. Mackenzie quotes 173—179° (see preceding paper), the actual figure depending very much on the rate of heating.

Mandelamidine mandelate crystallises in colourless plates, insoluble in ether, benzene, or light petroleum, sparingly soluble in water (100 grams dissolve 1·87 grams at 25°), rather more readily so in ethyl alcohol, and moderately so in methyl alcohol (100 grams dissolve 4·80 grams at 25°). It is comparatively unaffected by solvents, and can be recovered from them unchanged, whereas glycolliminohydrin recovered, for example, from a solution in hot alcohol, has always a decidedly lower melting point than the starting material.

Molecular Weight in Aqueous Solution (Cryoscopic Method).

Using 20 grams of solvent, the following data were obtained (K = 1870):

0·1210 gave $\Delta^t = -0·073$. M.W. = 155.
0·2348 „ $\Delta^t = -0·147$. M.W. = 149.

$C_{16}H_{18}O_4N_2$ requires M.W. = 302, hence at these dilutions the compound is almost completely ionised.

In boiling methyl alcohol (pure anhydrous), the following figures were obtained, using an electrically heated modification of Beckmann's apparatus, jacketed in a vacuum tube.

Weight of alcohol taken, 27·91 grams (K = 860).

0·5340 gave E = 0·080. M.W. = 206.
0·9923 „ „ = 0·150. M.W. = 204.
1·384 „ „ = 0·214. M.W. = 200.

As was to be expected, these figures indicate partial ionisation only of the compound in methyl alcohol.

Electrical Conductivity in Water at 25°.

As in the case of methoxyacetiminohydrin, the electrodes used were coated with "grey" platinum, but at the higher dilutions, $v = 400$ and above, oxidation was made apparent by the falling resistance of the cell. The solution at each dilution was freshly made up from an $N/20$-stock solution containing 1·511 grams in 100 c.c. The water used had a specific conductivity value of $1·4 \times 10^{-6}$ at 25°.

v	20	40	100	200	400	1000	2000
μ_{25}.....	43·0	46·0	51·0	53·0	54·4	55·2	56·2

"Mandeliminohydrin Hydrochloride."

The hydrolysis in aqueous solution of the "hydrochloride of glycolliminohydrin" was measured by Hantzsch by determining the electrical conductivity of a solution containing one molecular proportion of the bimolecular "iminohydrin" and two molecular proportions of hydrogen chloride. The figures obtained indicated extensive hydrolysis. As already stated, Walker, using the methyl acetate catalysis method, found almost exactly 50 per cent. of the hydrogen chloride in the uncombined state in $N/8$-solution. The hydrolysis of the mandelic compound, determined by the latter method, was again found to be 50 per cent. in $N/16$-solution. On the other hand, Eschweiler states (compare Hantzsch, *Ber.*, 1901, **34**, 3154) that glycolliminohydrin hydrochloride, obtained by evaporation of the solution of iminohydrin in hydrochloric acid, is a neutral salt having the structure $OH{\cdot}CH_2{\cdot}C(OH){:}NH,HCl$.

"Mandeliminohydrin," on being treated with excess of aqueous hydrochloric acid and evaporation in a vacuum over solid potassium hydroxide, was found to retain exactly a half-equivalent of acid, which could be estimated by titration with standard alkali in the presence of methyl-red. This solid hydrochloride showed no definite melting point, but "mandeliminohydrin," when dissolved in hot dilute hydrochloric acid, deposited, on cooling, well-formed crystals of a hydrochloride melting at 215—219°. These crystals proved to be neutral in aqueous solution, and evolved much ammonia with sodium hydroxide.

Action of Alkalis on "Mandeliminohydrin."

In the course of some experiments on the action of alkalis on "mandeliminohydrin," an aqueous solution of the latter was treated with exactly one molecular equivalent of sodium hydroxide. No ammonia could be detected after remaining for some minutes in the cold, but on warming the strongly alkaline solution, a considerable evolution of the gas was observed. The mixture was boiled until the evolution of ammonia ceased, when the residual liquid was found to be neutral. On cooling, a crop of crystals was deposited melting at 128—132°. These, after crystallisation from alcohol, melted at 131—132°, and proved to be pure mandelamide. The aqueous mother liquor contained sodium mandelate and yielded free mandelic acid on acidification. No other product could be detected.

These results suggested that the basic portion of the iminohydrin was set free by alkali and subsequently decomposed with

evolution of ammonia. Attempts to isolate a base soluble in ether were only successful when the aqueous alkali originally in use was replaced by a saturated solution.

When the finely powdered iminohydrin was rapidly shaken in a separating funnel with ether and saturated aqueous potassium hydroxide, the ethereal layer left, on evaporation in a vacuum, a very small amount of a white solid. This substance melted at 98—110°, was soluble in water, giving a powerfully alkaline solution, and after a short time decomposed, with the evolution of much ammonia. These properties are those of an amidine, mandelamidine, $C_6H_5\cdot CH(OH)\cdot C(NH_2){:}NH$ (Beyer, *J. pr. Chem.*, 1885, [ii], **31**, 383), melting at 110°. The neutral hydrochloride melting at 215—219° obtained above should then correspond with mandelamidine hydrochloride, $C_6H_5\cdot CH(OH)\cdot C(NH_2){:}NH,HCl$, which melts at 213—214° (Beyer). A specimen of the latter prepared from mandelimino-ethyl ether hydrochloride and alcoholic ammonia was found to melt at 219—220°.

The behaviour of "mandeliminohydrin" towards acids and alkalis, coupled with the characteristic reaction of glycolliminohydrin with calcium chloride, resulting in the deposition of calcium glycollate, pointed to these compounds being, in reality, amidine salts of the general type $R\cdot C(NH_2){:}NH,R\cdot CO_2H$.

Synthesis of "Mandeliminohydrin."

This constitution was readily confirmed by the formation of the "iminohydrin" on mixing in warm aqueous solution equivalent amounts of mandelamidine hydrochloride and sodium mandelate. On cooling, the solution deposited hard nodules melting and decomposing at 175—180°, which, after recrystallisation from alcohol, showed the characteristic plate formation of "mandeliminohydrin," and melted and decomposed at 184—186°.

Synthesis of "Glycolliminohydrin."

Equivalent amounts of sodium glycollate and glycollamidine hydrochloride (for preparation, see later) were mixed in aqueous solution. After evaporating to dryness, extraction with alcohol removed "glycolliminohydrin," melting at 166—168°.

"p-*Chloromandeliminohydrin*" (p-*Chloromandelamidine* p-*Chloromandelate*), $C_6H_4Cl\cdot CH(OH)\cdot C(NH_2){:}NH,C_6H_4Cl\cdot CH(OH)\cdot CO_2H$.

This compound was prepared for the purpose of comparing its physical constants with those of the mandelic derivative before the

constitution of the iminohydrins as amidine salts had been established. The preparation was a somewhat lengthy process, starting with the conversion of *p*-chlorotoluene into *p*-chlorobenzylidene chloride, $C_6H_4Cl{\cdot}CHCl_2$, by the action of chlorine on the boiling liquid under the influence of rays from a "Uviol" mercury-vapour lamp. The chloro-compound was heated in a sealed tube at 170° with water, yielding *p*-chlorobenzaldehyde, and the latter extracted with ether. The ethereal solution, after drying over sodium sulphate, was used direct for the preparation of *p-chloromandelimino-ethyl ether*, $C_6H_4Cl{\cdot}CH(OH){\cdot}C(OEt){:}NH$, by the method used above for the mandelic compound. Owing to the great tendency of the chloroaldehyde to oxidise in air, it was found necessary to carry out the reaction in closed vessels in an atmosphere of carbon dioxide. Twenty-four grams of *p*-chlorobenzylidene chloride gave 8 grams of the free imino-ether.

The compound crystallised from ether in well-defined plates melting at 107—109°. When recrystallised from light petroleum, it melted at 108—110°.

The crude product tends to oxidise in air, becoming red, but the pure substance can be kept for some weeks without much discoloration. It is sparingly soluble in water, soluble in dilute hydrochloric acid or alcohol, and readily so in hot benzene, from which it is precipitated by light petroleum.

An attempt to determine the chlorine content by Stepanov's method, using alcohol and metallic sodium, led to too high a figure being found, and it was noticed that decomposition of the imino-ether had taken place in such a way as to lead to the production of hydrogen cyanide.

Using the Carius-Volhard method, the following figures were obtained: 0·1172 gram was heated in a sealed tube with 0·2242 gram of silver nitrate and 2 c.c. of fuming nitric acid. After the reaction, the oxides of nitrogen were removed and the unchanged silver nitrate was titrated with thiocyanate, of which 7·35 c.c. (0·1052*N*) were required:

Cl = 16·5.

$C_{10}H_{12}O_2NCl$ requires Cl = 16·6 per cent.

"Chloromandeliminohydrin" was prepared, in small quantity only, by the method adopted in the case of the mandelic derivative. Continuous extraction of the dry product with ether separated the mixture into two portions.

p-*Chloromandelamide*, $C_6H_4Cl\cdot CH(OH)\cdot CO\cdot NH_2$.

The ethereal extract deposited a white, crystalline substance which, on crystallisation from benzene, melted at 122—123°. Analysis showed this to be the expected *p*-chloromandelamide. On hydrolysis with alkali, it yielded ammonia and a salt of chloromandelic acid.

0·1162 Gram heated with 0·2626 gram of silver nitrate and fuming nitric acid required for titration 9·10 c.c. of *N*/10-thiocyanate. Cl = 19·4.

$C_8H_8O_2NCl$ requires Cl = 19·1 per cent.

The amide is soluble in alcohol, sparingly so in ether, and very sparingly so in benzene. p-*Chloromandelamidine* p-*chloromandelate* was left behind in the crude state after extraction with ether as a white powder melting at 170—180°. Recrystallisation from a mixture of alcohol and benzene raised the melting point to 186—195° (with decomposition).

This compound proved to be unexpectedly unstable, and very readily decomposed with the evolution of ammonia on heating with solvents. Owing to its instability and the fact that its percentage composition does not differ from that of the amide with which it is liable to be contaminated, it was not further examined.

Treatment with dilute hydrochloric acid and subsequent recrystallisation from alcohol yielded the crystalline p-*chloromandelamidine hydrochloride*, $C_6H_4Cl\cdot CH(OH)\cdot C(NH_2){:}NH,HCl$, melting and decomposing at 252—253°:

0·3360 required 15·20 c.c. *N*/10-$AgNO_3$. Cl′ = 16·04.

$C_8H_9ON_2Cl,HCl$ requires Cl′ = 15·97 per cent.

Amidine Salts.

Some compounds of this type have been described by Eschweiler under the heading of "iminohydrin salts," but since much of the data furnished by this author is inaccurate, and since, moreover, he was under a misapprehension as to the structure of the compounds with which he was dealing, it was thought desirable to repeat certain of the preparations.

Glycollamidine Hydrochloride, $OH\cdot CH_2\cdot C(NH_2){:}NH,HCl$.

Eschweiler (*ibid.*) describes glycolliminohydrin hydrochloride as being prepared by the evaporation of a solution of the iminohydrin in an equivalent amount of dilute hydrochloric acid. The re-

crystallised product is quoted as melting at 135° and having the structure $OH{\cdot}CH_2{\cdot}C(OH){:}NH,HCl$.

Glycollamidine glycollate, prepared from the free imino-ether by treatment with water, gave, on evaporation with hydrochloric acid, a crude product melting at 130—150°. After repeated purification by solution in hot alcohol and precipitation with benzene, the hydrochloride was obtained in very fine needles melting at 150—151°.

In larger quantities, this salt was prepared from glycolliminoethyl ether hydrochloride and alcoholic ammonia according to the general method recommended by Pinner (*loc. cit.*). After purification from 98 per cent. alcohol, a product of the above melting point was obtained.

0·2003 was distilled with excess of sodium hydroxide and the ammonia trapped in 25 c.c. of 0·2036 *N*-sulphuric acid. The excess of acid required 7·70 c.c. of 0·1934 *N*-sodium hydroxide. N = 25·17.

0·1037 treated with 20 c.c. of *N*/10-silver nitrate required for titration 10·65 c.c. of *N*/10-ammonium thiocyanate. Cl = 31·97.

$C_2H_6ON_2,HCl$ requires N = 25·34; Cl = 32·08 per cent.

The salt is sparingly soluble in alcohol and practically insoluble in benzene or ether. It is very readily soluble in water and deliquescent in air.

Glycollamidine Sulphate, $(OH{\cdot}CH_2{\cdot}C(NH_2){:}NH)_2,H_2SO_4$.

Glycollamidine hydrochloride was treated with an equivalent of sulphuric acid, and the excess of water evaporated on the steam-bath. Recrystallisation from aqueous alcohol gave the sulphate in colourless leaflets melting and decomposing at 205°. Eschweiler (*loc. cit.*) gives 150° as the melting point of glycolliminohydrin sulphate, prepared in a similar manner:

0·2042 gave 0·1900 $BaSO_4$. S = 12·78.

$(C_2H_6ON_2)_2H_2SO_4$ requires S = 13·02 per cent.

The salt is not deliquescent, is readily soluble in water, and very sparingly so in absolute alcohol.

Glycollamidine Hydrogen Sulphate, $OH{\cdot}CH_2{\cdot}C(NH_2){:}NH,H_2SO_4$.

In order to ascertain if Eschweiler's sulphate, melting at 150°, were the hydrogen sulphate, glycollamidine hydrochloride was treated in aqueous solution with exactly two equivalents of sulphuric acid and evaporated to dryness in a vacuum over sodium hydroxide and sulphuric acid. The product was quite free from

chloride, and, after drying on porous porcelain in a vacuum, melted at 65—67° after having softened at 63°. On recrystallisation from aqueous alcohol, leaflets melting at 150—175° were deposited, which proved on analysis to contain more than 90 per cent. of the normal sulphate. Even from solvents containing a large excess of acid, the crystals deposited were mainly of the normal salt.

Glycollamidine Nitrate, $OH\cdot CH_2\cdot C(NH_2){:}NH,HNO_3$.

This substance was obtained by evaporating on the steam-bath equivalent amounts of glycollamidine hydrochloride and aqueous nitric acid. Recrystallisation from aqueous alcohol gave the pure nitrate, melting at 110—111° (Eschweiler gives 95° as the melting point of glycolliminohydrin nitrate).

A product melting at 110—111° was also obtained from glycollamidine glycollate (iminohydrin) and nitric acid:

0·2330 gave 0·1504 CO_2 and 0·1074 H_2O. C = 17·58; H = 5·15.
0·1497 „ 39·10 c.c. N_2 (dry) at 10·5° and 747 mm. N = 30·88.
$C_2H_6ON_2,HNO_3$ requires C = 17·52; H = 5·15; N = 30·68 per cent.

The salt is very readily soluble in water, and practically insoluble in absolute alcohol, benzene, or ether. From aqueous alcohol, it is deposited in leaflets which are stable in air.

Eschweiler's "lactiminohydrin sulphate" (lactamidine sulphate) is correctly quoted as melting at about 198°. A specimen prepared from the "iminohydrin" was found to melt and decompose at 200—202°. The hydrochloride and nitrate have already been described by Pinner.

Summary.

(1) The iminohydrins or *iso*amides, formulated by Eschweiler as $R\cdot C(OH){:}NH$, and by Hantzsch as $NH{:}CR\cdot O\cdot NH_2{:}CR\cdot OH$, have been shown to be amidine salts of the general type

$$R\cdot C(NH_2){:}NH,R\cdot CO_2H.$$

This structure has been confirmed by the synthesis of the mandelic compound and of Eschweiler's original "glycolliminohydrin."

(2) It is suggested that the production of amidine salt by the reaction between imino-ether and water takes place mainly through the intermediate formation of the ammonium salt of the corresponding acid, which by subsequent reaction with free imino-ether gives rise to the amidine salt.

(3) Certain inaccuracies of Eschweiler in reference to "iminohydrin" (amidine) salts have been corrected.

In conclusion, I desire to express my thanks to Professor Walker, at whose suggestion the above work was undertaken, for the interest he has shown throughout its course. I am also indebted to the Earl of Moray Research Fund for a grant which has covered most of the expenses in connexion with this research.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH. [*Received, July 2nd*, 1917.]

III.—*The Preparation of α-Naphtholphthalein.*

By EMIL ALPHONSE WERNER.

By heating phthalic anhydride with α-naphthol for a short time to the boiling point of the latter, Grabowski (*Ber.*, 1871, **4**, 661) obtained what was apparently an anhydride of α-naphtholphthalein. This substance, which had the composition $C_{28}H_{16}O_3$, was insoluble in alkalis, and was of no particular interest.

The true phthalein ($C_{28}H_{18}O_4$), which is readily soluble in alkalis with the production of an intense pure blue colour, was shortly afterwards obtained by Grabowski (*Ber.*, 1871, **4**, 725; 1873, **6**, 1065) from the interaction of α-naphthol and phthalyl chloride.

Sörensen and Palitzsch (*Biochem. Zeitsch.*, 1910, **24**, 381) have directed attention to the great delicacy of α-naphtholphthalein as an indicator in alkalimetry, and have described in detail a method for its preparation, which differs but little from that recorded by Grabowski.

Having recently received a request from one of my colleagues for a small quantity of this indicator, which apparently is difficult to procure at the present time, a few experiments were made in order to ascertain if the substance could be prepared with the aid of phthalic anhydride, which is so generally employed in the preparation of other phthaleins.

Conditions necessary for obtaining the compound in very good yield were soon established, and since α-naphtholphthalein has some special application in biochemistry, it may be of interest, and a saving of time, to others to place on record the following details of its preparation.

The most successful experiment was conducted as follows. An intimate mixture of 7 grams of α-naphthol and 3·8 grams of powdered phthalic anhydride was introduced into a stout, wide-mouthed test-tube, and 0·75 c.c. of concentrated sulphuric acid was

added. The tube, which carried a thermometer, was partly immersed in a beaker half full of water, and heat was applied until the contents of the tube had reached 60°; the heating was maintained for four hours, during which period the temperature was never allowed to rise above 65°. The mixture was well stirred at intervals by means of the thermometer.

The dark greenish-black, viscous product was extracted with water until free from sulphuric acid, after which the semi-solid mass was digested at about 70° with a litre of 0·5 per cent. solution of sodium hydroxide until the extraction of all material soluble in the alkali had been completed. The weight of pale yellow, insoluble matter (Grabowski's 'anhydride') was only 0·8 gram. To the deep blue solution obtained, after filtration, dilute hydrochloric acid in quantity sufficient to neutralise about one-half of the sodium hydroxide present was added, after which the liquid was saturated with carbon dioxide. The pale reddish-brown precipitate of α-naphtholphthalein was collected, washed, redissolved in dilute solution of sodium hydroxide, and reprecipitated as before. The weight obtained after drying in a vacuum over sulphuric acid was 2·3 grams, equal to nearly 33 per cent. of the weight of α-naphthol taken. Sörensen and Palitzsch, using phthalyl chloride, obtained a yield equal to 30·5 per cent. calculated on the same basis.

In order to ensure a successful result in the preparation of α-naphtholphthalein by the method just described, great care must be taken to avoid a rise of temperature above 65°. Thus, when the temperature was maintained at 70—80°, the yield was only about one-half of that obtained at 65°, whilst at 80—90°, Grabowski's 'anhydride' was almost the sole product.

Excess of sulphuric acid was also found greatly to promote the formation of the anhydride at the expense of the phthalein.

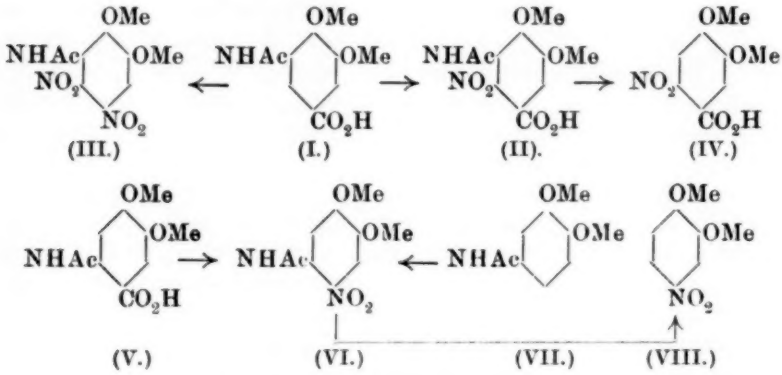
Attempts to hydrolyse Grabowski's anhydride to α-naphtholphthalein by heating with dilute acids or alkalis under the ordinary pressure or in sealed tubes were unsuccessful.

UNIVERSITY CHEMICAL LABORATORY,
TRINITY COLLEGE, DUBLIN. [*Received, November 5th*, 1917.]

IV.—*The Nitration of* 5- *and* 6-*Acetylamino*-3:4-*dimethoxybenzoic Acids and* 4-*Acetylaminoveratrole.*

By JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU.

THE nitration of 2-acetylamino-3:4-dimethoxybenzoic acid and 3-acetylaminoveratrole was investigated by Gibson, Simonsen, and Rau (T., 1917, **111**, 69), and in view of the results obtained it appeared to us desirable to examine the products formed by the nitration of the two isomeric acetylamino-3:4-dimethoxybenzoic acids and of 4-acetylaminoveratrole.



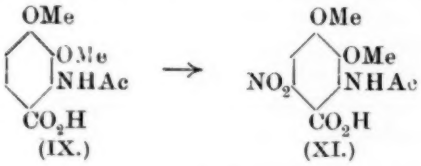
5-*Acetylamino*-3:4-*dimethoxybenzoic acid* (I), which was found to be most conveniently prepared from 5-nitrovanillin under the conditions described in the experimental part of this paper, when treated with nitric acid gave a mixture of a nitroacetylamino-acid and a neutral substance which was insoluble in sodium carbonate solution. The latter substance was found to be 4:5-dinitro-3-acetylaminoveratrole (III), a substance already described (*loc. cit.*, p. 78). The nitroacetylamino-acid was readily shown to be 6-*nitro*-5-*acetylamino*-3:4-*dimethoxybenzoic acid* (II), since the *amino*-acid obtained from it on hydrolysis yielded, when diazotised in alcoholic solution, 6-nitroveratric acid (IV).

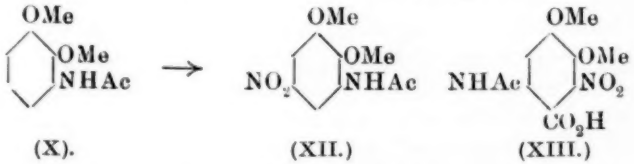
When 6-*acetylamino*-3:4-*dimethoxybenzoic acid* (V) was nitrated, it was not found possible to avoid the displacement of the carboxyl group, and the sole product of the reaction was 5-*nitro*-4-*acetylaminoveratrole* (VI). The same substance was also obtained by the nitration of 4-acetylaminoveratrole (VII). The constitution of the nitroacetylaminoveratrole was proved by the fact that when

the amino-group was displaced by hydrogen, 4-nitroveratrole (VIII) was obtained.

If these results are considered in the light of the suggestions made by the authors (T., 1917, **111**, 224), it will be observed that the nitration of 5-acetylamino-3:4-dimethoxybenzoic acid proceeds exactly as might be expected. In the formation of the nitroacetylamino-acid, which is evidently the primary product of the reaction, the negative carboxyl group appears to exercise no direct orientating effect except in so far as it neutralises the methoxy-group in the para-position with respect to it; the first nitro-group enters the ortho-position with respect to the acetylamino-group and the para-position with respect to the second methoxy-group. There appears to be no tendency for the elimination of a methoxy-group to take place, as has been observed by various investigators in somewhat analogous cases, and further nitration of the nitroacetylamino-acid merely results in the displacement of the carboxyl group with the formation of 4:5-dinitro-3-acetylaminoveratrole.

The result obtained in the case of the 6-acetylamino-acid was somewhat unexpected. In view of the fact that both in the case of 2-acetylamino-3:4-dimethoxybenzoic acid (IX) and of 3-acetylaminoveratrole (X) the nitro-group enters the para-position with respect to the methoxy-group which was in the ortho-position with respect to the acetylamino-group, it was thought that the 6-acetylamino-acid would yield the 2-nitro-derivative (XIII).





This did not prove to be the case, displacement of the carboxyl group by the nitro-group taking place. This indicates clearly that an acetylamino-group exercises much less influence on a methoxy-group when in the para-position with respect to it than when in the ortho. This view was supported by the fact that 4-acetylaminoveratrole gave on nitration an excellent yield of 5-nitro-4-acetylaminoveratrole (VI), no trace of an isomeride being formed.

Experimental.

5-Amino-3:4-dimethoxybenzoic Acid.

For the preparation of this acid, the following method was found to yield the most satisfactory results (compare Hayduck, *Ber.*, 1903, **36**, 2930). Vanillin (10 grams) was dissolved in ether (200 grams), and a steady stream of oxides of nitrogen (prepared by the action of dilute sulphuric acid on sodium nitrite) was led through the well-cooled solution for two to three hours. After the addition of a little water, the mixture was allowed to remain overnight, when 5-nitrovanillin crystallised out. This was collected, and after washing with a little ether, in which it was only very sparingly soluble, it was found to be pure, melting at 175—176°. The yield was 8 grams.

The methylation of 5-nitrovanillin offered considerable difficulty, and ultimately the following method was adopted. The finely powdered potassium salt (dried at 130°) was suspended in dry toluene, and, after the addition of a slight excess of methyl sulphate, the mixture was heated at 135—140° for two to three hours in an oil-bath, when the scarlet potassium salt was completely decomposed. The toluene was removed by distillation in a current of steam, and the mixture of 5-nitroveratrole and 5-nitrovanillin was collected and triturated with dilute sodium hydroxide solution, when pure 5-nitroveratrole was obtained, the yield being 50 per cent of the theoretical. By oxidation with potassium permanganate in alkaline solution, a quantitative yield of 5-nitro-3:4-dimethoxybenzoic acid was obtained.

The barium salt of the nitro-acid was readily reduced by means of an alkaline solution of ferrous hydroxide in the usual manner. On concentrating the solution of the barium salt of the amino-acid to a small bulk and rendering strongly acid with concentrated hydrochloric acid, the *hydrochloride* separated in a yield of 50 per cent. of the theoretical. The hydrochloride was purified by crystallisation from a mixture of moist acetone and ethyl acetate or by solution in alcohol and precipitation with concentrated hydrochloric acid, when it was obtained in woolly needles decomposing at 235°:

0·1094 gave 0·0694 AgCl. Cl = 15·6.

$C_9H_{11}O_4N,HCl$ requires Cl = 15·2 per cent.

Attempts to prepare a pure specimen of the amino-acid from the hydrochloride were unsuccessful, the amino-acid darkening with extreme readiness on exposure to the air.

The *platinichloride* separated in fine, glistening, yellow needles

which were readily soluble in water. It possessed no definite melting point, but became brown at about 180° and gradually blackened. It was not melted at 270°. For analysis it was dried at 100°:

0·1799 gave 0·0432 Pt. Pt = 24·0.

$(C_9H_{11}O_4N)_2,H_2PtCl_6$ requires Pt = 24·2 per cent.

5-Acetylamino-3 : 4-dimethoxybenzoic acid (I), prepared in the usual manner from the hydrochloride, separated from hot water in glistening, fine needles containing one molecule of water of crystallisation, which was lost on drying at 100°. It softened at 117° and melted at 126°, the anhydrous substance melting at 188°:

*0·4385 lost 0·0314 H_2O at 100°. H_2O = 7·2.

†0·1059 gave 0·218 CO_2 and 0·0511 H_2O. C = 55·3; H = 5·4.

$C_{11}H_{13}O_5N,H_2O$ requires H_2O = 7·0 per cent.

$C_{11}H_{13}O_5N$ requires C = 55·2; H = 5·4 per cent.

Nitration of 5-Acetylamino-3 : 4-dimethoxybenzoic Acid. 6-Nitro-5-acetylamino-3 : 4-dimethoxybenzoic Acid (II), *and 4 : 5-Dinitro-3-acetylaminoveratrole* (III).

In one experiment, 5-acetylamino-3 : 4-dimethoxybenzoic acid (2 grams) was gradually added to nitric acid (D 1·52; 6 grams), which was kept well cooled in a mixture of salt and ice. The reaction proceeded with considerable evolution of gas, and after ten minutes the extremely viscid, yellow liquid was poured on ice, when an oil separated which gradually solidified. The solid was collected, washed with a little ice water, and triturated with a dilute solution of sodium carbonate. The insoluble residue (0·9 gram) was crystallised from acetic acid, when it was obtained in glistening needles melting at 241°, and was found to consist of 4 : 5-dinitro-3-acetylaminoveratrole, identical in every respect with the substance described by Gibson, Simonsen, and Rau (T., 1917, **111**, 78). (Found, N = 15·1. Calc., N = 14·7 per cent.).

The alkaline solution from which the dinitro-compound had been separated was acidified, when the *nitroacetylamino-acid* was precipitated in pale brownish-yellow crystals (1·2 grams). It was purified by crystallisation from dilute alcohol:

0·143 gave 14 c.c. N_2 at 32° and 760 mm. N = 10·3.

$C_{11}H_{12}O_7N_2$ requires N = 9·9 per cent.

6-Nitro-5-acetylamino-3 : 4-dimethoxybenzoic acid crystallises in straw-coloured needles which decompose at 220—221°. It is readily soluble in alcohol or acetone, very sparingly so in water, benzene, chloroform, or ethyl acetate, but more readily so in hot water.

* Air dried. † Dried at 100°.

When heated on the water-bath with hydrochloric acid (50 per cent.) for some hours, it gradually passed into solution, and on neutralising the excess of mineral acid with ammonia, the *amino*-acid separated as a pale yellow, crystalline powder. It was recrystallised from a mixture of ethyl acetate and benzene:

0·13 gave 15 c.c. N_2 at 30° and 760 mm. N = 12·4.

$C_9H_{10}O_6N_2$ requires N = 12·2 per cent.

6-*Nitro*-5-*amino*-3 : 4-*dimethoxybenzoic acid* crystallises in iridescent yellow, prismatic needles which melt at 148°.* It is readily soluble in acetone, ethyl acetate, or alcohol, but very sparingly so in water or benzene.

Diazotisation of 6-*Nitro*-5-*amino*-3 : 4-*dimethoxybenzoic Acid.* 6-*Nitro*-3 : 4-*dimethoxybenzoic Acid* (IV).

The amino-acid (0·5 gram) was dissolved in alcohol (5 c.c.), and, after the addition of sulphuric acid (1 gram), amyl nitrite (1 gram) was added to the well-cooled mixture. The clear solution gradually became cloudy, and after some minutes the sparingly soluble diazonium salt crystallised. This was decomposed on the water-bath, and on pouring into water a reddish-yellow solid separated, which was found to be a mixture of 6-nitro-3 : 4-dimethoxybenzoic acid and a phenolic acid. It was therefore dissolved in alkali and methylated with methyl sulphate in the usual manner, treated with potassium permanganate to remove a trace of phenolic acid, and the solution filtered and concentrated, when, on acidifying, the nitro-acid was obtained as a caseous, white precipitate. It was recrystallised from hot water, when it was obtained in fine needles melting at 185—187°, and this melting point was unaltered on admixture with a specimen of the 6-nitro-acid from another source. As a further proof of the constitution of this acid, the methyl ester was prepared. It crystallised in fine needles melting at 143—144°, which is the melting point of methyl 6-nitro-3 : 4-dimethoxybenzoate.

6-*Acetylamino*-3 : 4-*dimethoxybenzoic Acid* (V).

This substance, which does not seem to have been prepared previously, was readily obtained when the hydrochloride of the amino-acid (*Ber.*, 1876, **9**, 942) was warmed with acetic anhydride. It was crystallised from dilute acetic acid, when it was obtained in colourless, irregular prisms decomposing at 228°:

* On one occasion a trace of an acid was isolated which crystallised in plates and melted at about 180°. It was probably the isomeric nitro-acid but it was not obtained in sufficient quantity for analysis.

0·1857 gave 10·4 c.c. N_2 at 30° and 760 mm. N = 6·6
$C_{11}H_{13}O_5N$ requires N = 5·9 per cent.

Nitration of 6-Acetylamino-3 : 4-dimethoxybenzoic Acid. 5-Nitro-4-acetylaminoveratrole (VI).

A large number of experiments were made with the view of finding a method for nitrating the amino-acid without the elimination of the carboxyl group, but in this we were unsuccessful. In one experiment, the finely powdered acetylamino-acid (2 grams) was slowly added to nitric acid (D 1·42; 6 grams), well cooled in a mixture of salt and ice. The acid dissolved with the evolution of gas, and in a short time the whole mass became pasty owing to the separation of the nitro-derivative. After fifteen minutes, the mixture was poured on ice, and the yellow solid collected (2 grams). It was found to be quite homogeneous, and was purified by crystallisation from alcohol:

0·1061 gave 11·8 c.c. N_2 at 30° and 759 mm. N = 11·9.
$C_{10}H_{12}O_5N_2$ requires N = 11·7 per cent.

5-Nitro-4-acetylaminoveratrole separates from alcohol in golden-yellow needles melting at 196°. It is insoluble in water, sparingly soluble in cold alcohol or acetic acid, but more readily so in hot alcohol or acetic acid.

5-Nitro-4-aminoveratrole.—This substance was readily obtained when the foregoing compound was dissolved in sulphuric acid (90 per cent.) and the solution heated at 100° for ten minutes. On pouring into water, the *nitroamine* separated as a yellow powder, and was purified by crystallisation from alcohol:

0·1054 gave 14 c.c. N_2 at 30° and 759 mm. N = 14·3.
$C_8H_{10}O_4N_2$ requires N = 14·1 per cent.

5-Nitro-4-aminoveratrole crystallises in terra-cotta-coloured needles melting at 171°. It is readily soluble in acetone, hot alcohol, or hot ethyl acetate, but very sparingly so in benzene or chloroform. It dissolves readily in concentrated mineral acids, but is reprecipitated on dilution. The high melting point of this nitroamine is somewhat remarkable, and in order to make certain that no change had taken place on hydrolysis, it was treated with acetic anhydride, when the acetyl derivative melting at 196° was obtained.

The benzoyl derivative crystallised from alcohol in sulphur-yellow, woolly needles melting at 153—154°.

When diazotised with amyl nitrite in alcoholic solution in the usual manner, the nitroamine gave a nearly quantitative yield of 4-nitroveratrole melting at 95—96°. (Found, N = 7·6. Calc.,

N = 7·6 per cent.) There can therefore be no doubt as to its constitution.

4-Aminoveratrole.

The preparation of 4-aminoveratrole by the reduction of 4-nitroveratrole offered some difficulty owing to the tendency for chlorination to take place simultaneously. Ultimately, the following method was found to give fairly satisfactory results. 4-Nitroveratrole (10 grams) was mixed with tin (16 grams), and, after the addition of a trace of graphite (compare Pinnow, *J. pr. Chem.*, 1901, [ii], **63**, 352), hydrochloric acid (50 c.c. of 50 per cent.) was added, and the mixture heated on the water-bath for from two to three hours. The yield of 4-aminoveratrole, isolated in the usual manner, was about 50 per cent. of the theoretical.

Nitration of 4-Acetylaminoveratrole.

To nitric acid (D 1·4; 6 grams), well cooled in a mixture of salt and ice, finely powdered 4-acetylaminoveratrole [VII] (2 grams) was gradually added. The nitration proceeded with considerable evolution of gas, and in a short time the whole mass became pasty. After fifteen minutes, the mixture was poured on ice, when a yellow solid separated. This was collected, and found to melt at 195° (1·4 grams). It was crystallised from alcohol, when it was obtained in golden-yellow needles melting at 196°, and was found to be identical in every respect with the 5-nitro-4-acetylaminoveratrole obtained by the nitration of 6-acetylamino-3:4-dimethoxybenzoic acid (see above):

0·0727 gave 0·1337 CO_2 and 0·0352 H_2O. C = 50·1; H = 5·3.
$C_{10}H_{12}O_5N_2$ requires C = 50·0; H = 5·0 per cent.

THE PRESIDENCY COLLEGE,
MADRAS.

[*Received, November 6th*, 1917.]

V.—*Studies in Phototropy and Thermotropy. Part VIII. Cinnamylideneamines. 2:4-Dihydroxybenzylideneamines.*

By ALFRED SENIER and PATRICK HUGH GALLAGHER.

THIS communication is a report of further study of the condensation products of aromatic aldehydes with amines, the anils, or Schiff's bases, with a view to the discovery and special examination of such as might exhibit phototropic or thermotropic change.

Previous communications have shown that whilst compounds of this class are generally thermotropic, they are not phototropic unless they contain an hydroxyl group in an ortho-position with respect to the aldehyde group of the benzylidene nucleus. Moreover, the property appears to be inhibited by the entry into the nucleus of such substituents as bromine, methyl, or methoxyl.

With one possible exception (Foresti, *Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 270), phototropy has not been observed except in the case of solids, and it has been suggested (Senier and Shepheard, T., 1909, **95**, 1944) that it is not due to intramolecular change, but to reversible extra-molecular rearrangement of the molecules into molecular aggregates. In order to determine, if possible, whether this explanation or some other is the true one, we are endeavouring to discover further instances of phototropic compounds for study.

We wished to examine the 2-hydroxycinnamylideneamines, but practical difficulties at the present time have prevented us. This paper contains, however, an account of the preparation and investigation of the simpler cinnamylideneamines, and also of 2:4-dihydroxybenzylideneamines, which latter contain, in addition to an *o*-hydroxyl group, another hydroxyl group in the *p*-position.

None of the compounds is phototropic between "the lower temperature," that of solid carbon dioxide, and "the higher temperature," just below their melting points. Prolonged exposure to actinic light, however, induces permanent *polymorphic* change in many instances. Thermotropy was detected in nearly all cases. Differences of colour in solution depending on the solvent employed were generally observed. The solutions in acetic acid or chloroform were usually deeper in colour than those in light petroleum, benzene, or acetone (compare Senier and Shepheard, T., 1909, **95**, 1943). Trituration appears to yield a *polymorphic variety* in the case of cinnamylidene-*m*-bromoaniline, but was not otherwise observed. No tritoluminescence was detected.

The 2:4-dihydroxybenzylidene derivatives exhibit marked *dichroism* in solution. They are green in very thin layers or in dilute, and yellow in thicker layers or when the solutions are concentrated. The green colour of thin layers appears to partake of the character of fluorescence, for it persists when viewed with light from a blue or violet light-filter.

Most of the compounds are readily formed by mixing alcoholic solutions of the aldehyde and base. The ortho-substituted anilines, however, combine with the aldehydes only on prolonged heating at 100°. Attempts to prepare mono-derivatives of phenylene- and naphthylene-diamines resulted in the formation of di-derivatives.

The source of actinic light employed was direct sunlight or a mercury lamp. The compounds dissolve generally in the usual organic solvents; any important exception is noted.

Cinnamylideneaniline, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C_6H_5$ (Döbner and Miller, *Ber.*, 1883, **16**, 1665), consists of yellow plates which melt at 109° (corr.). It is changed into a deeper coloured *polymorphic form* by the prolonged action of actinic light, and is thermotropic at both "the higher" and "the lower temperatures."

Cinnamylidenechloroanilines, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C_6H_4Cl$.

Cinnamylidene-o-chloroaniline at first separates mixed with tarry matter, which may be removed by careful washing with alcohol, light petroleum, or ether. After several crystallisations, it becomes nearly colourless, the crystals showing a pale greenish-yellow tinge. It melts at 63·5° (corr.):

0·1324 gave 7 c.c. N_2 at 17° and 767 mm. N = 5·96.
$C_{15}H_{12}NCl$ requires N = 5·80 per cent.

This compound shows no change of colour by the action of actinic light or by changes of temperature.

Cinnamylidene-*p*-chloroaniline (James and Judd, T., 1914, **105**, 1430) crystallises in pale yellow or, as in our experiment, in nearly colourless plates which melt at 107° (corr.). It is not phototropic, but exhibits thermotropy at "the higher," and in a less degree at "the lower temperatures."

Cinnamylidenebromoanilines, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C_6H_4Br$.

Cinnamylidene-o-bromoaniline separates from alcoholic solution in pale greenish-yellow clusters which melt at 74° (corr.):

0·1668 gave 7·1 c.c. N_2 at 19° and 762 mm. N = 4·98.
$C_{15}H_{13}NBr$ requires N = 4·88 per cent.

Slight thermotropy was detected both above and below the ordinary temperature.

Cinnamylidene-*m*-bromoaniline (James and Judd, T., 1914, **105**, 1434) consists of pale yellow plates which melt at 122° (corr.). (The above authors found 115—116°.) Prolonged action of actinic light produces a slight permanent deepening of colour, and slight evidence of thermotropy was observed.

Cinnamylidene-p-*bromoaniline* crystallises from alcohol, chloroform, or benzene in pale greenish-yellow plates which melt at 120° (corr.). A permanent deepening in colour occurs when this com-

pound is submitted to the prolonged action of actinic light, and thermotropy was observed at "the lower temperature."

0·1402 gave 5·9 c.c. N_2 at 16° and 768 mm. N = 4·885.
$C_{15}H_{13}NBr$ requires N = 4·88 per cent.

Cinnamylidenetoluidines, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C_6H_4Me$.

Cinnamylidene-*o*-toluidine (James and Judd, T., 1914, **105**, 1433), which melts at 73°, is not affected by actinic light or by temperature changes under its melting point.

Cinnamylidene-*m*-toluidine is neither phototropic nor thermotropic (Senier and Shepheard, T., 1909, **95**, 1955).

Cinnamylidene-*p*-toluidine (Tinkler, T., 1913, **103**, 894) consists of pale greenish-yellow plates which melt at 83° (corr.). Slight deepening of colour occurred by the prolonged action of actinic light. No evidence of thermotropy was observed.

Cinnamylidenenitrotoluidines, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C_6H_3Me{\cdot}NO_2$.

Cinnamylidene-4-*nitro*-o-*toluidine* forms pale greenish-yellow clusters which melt at 126° (corr.):

0·1140 gave 10·4 c.c. N_2 at 19° and 757 mm. N = 10·54.
$C_{16}H_{15}O_2N_2$ requires N = 10·50 per cent.

This compound forms deeper coloured solutions in alcohol or acetic acid than in the other ordinary solvents. It is not phototropic, but is thermotropic at "the higher temperature."

Cinnamylidene-2-*nitro*-p-*toluidine* crystallises from alcohol in pale yellow leaflets which melt at 108° (corr.):

0·2388 gave 21·2 c.c. N_2 at 15° and 767 mm. N = 10·58.
$C_{16}H_{15}O_2N_2$ requires N = 10·50 per cent.

This compound is not affected by actinic light, but exhibits thermotropy at both "the higher" and "the lower temperatures."

Cinnamylidene-*m*-nitroaniline (James and Judd, 1914, **105**, 1434) is not thermotropic, nor is it affected by actinic light.

Cinnamylidene-p-*anisidine*, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}OMe$, is obtained from solutions in alcohol in large yellow plates which melt at 119° (corr.):

0·1106 gave 5·6 c.c. N_2 at 16° and 759 mm. N = 6·00.
$C_{16}H_{15}ON$ requires N = 5·93 per cent.

This base dissolves sparingly in cold alcohol. Acetic acid changes the yellow crystals into a scarlet, probably *dimorphic variety*, which we propose to examine further. It is not affected

by actinic light, but is slightly thermotropic at "the lower temperature."

Cinnamylidene-p-phenetidine, $C_6H_5\cdot CH{:}CH\cdot CH{:}N\cdot C_6H_4\cdot OEt$, consists of pale green, lustrous plates which melt at 108° (corr.). Like the preceding base, acetic acid changes it into a red *dimorphic variety*, which crystallises in prisms. It is slightly thermotropic, but is not phototropic:

0·1328 gave 6·2 c.c. N_2 at 15° and 767 mm. N = 5·58.
$C_{17}H_{17}ON$ requires N = 5·58 per cent.

Cinnamylidene-p-xylidine, $C_6H_5\cdot CH{:}CH\cdot CH{:}N\cdot C_6H_3Me_2$, separates in pale yellow needles which melt at 111·5° (corr.):

0·0856 gave 4·3 c.c. N_2 at 15° and 764 mm. N = 6·08.
$C_{17}H_{17}N$ requires N = 5·95 per cent.

This compound is not affected by actinic light, but exhibits slight thermotropy at both "the higher" and "the lower temperatures."

Cinnamylidene-ψ-cumidine, $C_6H_5\cdot CH{:}CH\cdot CH{:}C_6H_2Me_3$ (Schiff, *Annalen*, 1887, **239**, 384), which melts at 105°, is not affected by actinic light, but is thermotropic at both "the higher" and "the lower temperatures."

Cinnamylidenenitro-ψ-cumidine,
$C_6H_5\cdot CH{:}CH\cdot CH{:}N\cdot C_6HMe_3\cdot NO_2$
—This base separates at first in orange-red needles. After several recrystallisations, yellow crystals are obtained, which revert to orange-red on keeping. After further recrystallisations, however, the product retains its yellow colour. It melts at 117° (corr.). Actinic light has no effect on this base, nor is it thermotropic:

0·2424 gave 20 c.c. N_2 at 17° and 759 mm. N = 9·63.
$C_{18}H_{18}O_2N_2$ requires N = 9·53 per cent.

Cinnamylidene-β-naphthylamine, $C_6H_5\cdot CH{:}CH\cdot CH{:}N\cdot C_{10}H_7$ (Schiff, *Annalen*, 1887, **239**, 384), is stated to melt at 95—96°. Our specimen melts at 124° (corr.). (Found, N = 5·41. $C_{19}H_{15}N$ requires N = 5·46 per cent.)

This base is neither phototropic nor thermotropic, but by the prolonged action of actinic light it changes into a deeper coloured *polymorphic form*.

Cinnamylidenecamphylamine was prepared, but as it proved to be a liquid and the quantity was small, we did not proceed with it further.

Dicinnamylidene-p-phenylenediamine,
$(C_6H_5\cdot CH{:}CH\cdot CH{:}N)_2C_6H_4$,

separates from alcohol as a pale yellow powder which melts at 209° (corr.). It is not phototropic or thermotropic:

0·1802 gave 12·6 c.c. N_2 at 17° and 760 mm. N = 8·04.
$C_{24}H_{20}N_2$ requires N = 8·34 per cent.

Dicinnamylidene-o-naphthylenediamine,
$(C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}N)_2C_{10}H_6$,
separates readily in brick-red crystals, but on being left in contact with the solvent, they change into a viscous, red tar. By quickly recrystallising several times from alcohol, and subsequently washing with ether and drying, the compound melts at 136° (corr.):

0·1364 gave 8·7 c.c. N_2 at 21° and 766 mm. N = 7·66.
$C_{26}H_{22}N_2$ requires N = 7·74 per cent.

This compound dissolves in the usual organic solvents, giving blood-red solutions; the solutions in ethyl, methyl, or amyl alcohols, and in ether, ethyl acetate, or acetone, exhibit a strong blue fluorescence; those in toluene or xylene are slightly fluorescent; those in benzene or nitrobenzene are not fluorescent. On keeping, even in the dry state, this base changes into a *dimorphic variety* of a yellowish-grey colour which melts at 112° (corr.). When dissolved, this modification appears to revert to the original compound.

Dicinnamylidenebenzidine, $(C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C_6H_4)_2$ (Schiff, *Annalen*, 1887, **239**, 385), is obtained easily as a yellow powder. It melts at 249° (corr.). Acetic acid dissolves it, forming a red solution, but it is only sparingly soluble in the other organic solvents. It is thermotropic at "the higher temperature," but is not affected by actinic light:

0·1098 gave 6·4 N_2 at 16° and 768 mm. N = 6·92.
$C_{30}H_{24}N_2$ requires N = 6·80 per cent.

2:4-*Dihydroxybenzylideneaniline*, $(OH)_2C_6H_3{\cdot}CH{:}N{\cdot}C_6H_5$, forms pale greenish-yellow needles from solution in most organic solvents. It melts at 99·5° (corr.) (Dimroth and Zoeppritz, *Ber.*, 1902, **35**, 995, give 125—126°, and Gattermann, *Annalen*, 1907, **357**, 336, gives 131°). (Found, N = 6·39. $C_{13}H_{11}O_2N$ requires N = 6·57 per cent.)

This compound is thermotropic, both at the higher and the lower temperatures; it is not phototropic, but changes into a deeper coloured *polymorphic form* on prolonged exposure to actinic light.

2:4-*Dihydroxybenzylidene-o-bromoaniline*,
$(OH)_2C_6H_3{\cdot}CH{:}N{\cdot}C_6H_4Br$.
—The product consisted of a reddish-yellow tar, which eventually solidified, and yielded by treatment with solvents a reddish-yellow,

amorphous powder; this separated from benzene solution in crystals melting at 91° (corr.):

0·1210 gave 5·0 c.c. N_2 at 22° and 762 mm. N = 4·68.

$C_{13}H_{10}O_2NBr$ requires N = 4·79 per cent.

This compound is thermotropic both at "the higher" and "the lower temperatures," and yields a *polymorphic form* by long exposure to actinic light, but is not phototropic.

2:4-*Dihydroxybenzylidene*-m-*bromoaniline*.—The first product of the reaction is a deep red liquid which soon solidifies. The substance separates from benzene solution in deep yellow crystals melting at 111·5° (corr.):

0·2829 gave 11·8 c.c. N_2 at 15° and 751 mm. N = 4·86.

$C_{13}H_{10}O_2NBr$ requires N = 4·79 per cent.

The yellow crystals are changed into a red *dimorphic form* by contact with acetic acid or benzene, and an orange-coloured product was noticed on prolonged exposure to actinic light and also on trituration. It is not phototropic, but exhibits thermotropy at "the lower temperature."

2:4-*Dihydroxybenzylidene*-p-*bromoaniline* crystallises in pale greenish-yellow needles from alcohol, chloroform, or acetone, or in plates from acetic acid or benzene. It melts at 124° (corr.):

0·1840 gave 7·6 c.c. N_2 at 16° and 751 mm. N = 4·78.

$C_{13}H_{10}O_2NBr$ requires N = 4·79.

This base is not phototropic, but changes to a deeper coloured *polymorphic form* on long exposure to actinic light. It is thermotropic at both "the higher" and "the lower temperatures."

2:4-*Dihydroxybenzylidene*-m-*toluidine*,

$(OH)_2C_6H_3{\cdot}CH{:}N{\cdot}C_6H_4Me$.

—The first product of the reaction consisted of a mass of scarlet crusts and yellow needles (*dimorphic forms*). On recrystallisation, the whole separated in yellow needles, which melt at 137° (corr.):

0·0976 gave 5·1 c.c. N_2 at 20° and 762 mm. N = 6·05.

$C_{14}H_{13}O_2N$ requires N = 6·17 per cent.

This compound is thermotropic both at "the higher" and "the lower temperatures"; it is not phototropic, but acted on by actinic light yields a deeper coloured *polymorphic form*.

2:4-*Dihydroxybenzylidene*-β-*naphthylamine*,

$(OH)_2C_6H_3{\cdot}CH{:}N{\cdot}C_{10}H_7$,

separates from acetone in yellow needles or from alcohol in yellow plates. It melts at 160·5° (corr.):

0·1220 gave 5·6 c.c. N_2 at 20° and 762 mm. N = 5·31.

$C_{17}H_{13}O_2N$ requires N = 5·32 per cent.

This compound is not affected by actinic light, but is thermotropic at the higher temperature, changing to an orange thermotrope.

2:4-*Dihydroxybenzylidenecamphylamine*,

$$(OH)_2C_6H_3\cdot CH{:}N\cdot CH_2\cdot C_9H_{15}.$$

—Pale greenish-yellow needles of this compound separate from solutions in alcohol, chloroform, benzene, or acetone. These melt at 133° (corr.). In acetic acid it dissolves, forming a colourless solution—a *dimorphic form*—but from this solution we were only able to obtain a small quantity of a yellow oil. The yellow needles are not phototropic, but are slightly thermotropic both at "the higher" and at "the lower temperatures":

0·1537 gave 7 c.c. N_2 at 15° and 768 mm. N = 5·04.

$C_{17}H_{23}O_2N$ requires N = 5·13 per cent.

UNIVERSITY COLLEGE,
GALWAY.

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VI.—*Studies on the Sulphonation of β-Naphthylamine.*

By ARTHUR GEORGE GREEN and KAPILRAM H. VAKIL.

THE isomeric β-naphthylaminesulphonic acids are of considerable importance in the dye industry partly as such and partly for the preparation of other intermediate compounds. It therefore appeared to be of interest to submit the sulphonation of β-naphthylamine to a more detailed study than has yet been published, directed to ascertaining the mechanism of the reactions involved, the circumstances favouring the production of the respective isomerides, and the conditions for the conversion of one into another.

Previous workers have shown (Badische Anilin- & Soda-Fabrik, D.R.-P., 20760; Dahl & Co., E.P., 7712 of 1884; Bayer and Duisberg, *Ber.*, 1887, **20**, 1426; Forsling, *Ber.*, 1886, **19**, 1815; 1887, **20**, 2103; Green, T., 1889, **55**, 33) that the sulphonation of β-naphthylamine gives rise to four monosulphonic acids, originally distinguished by the prefixes α, β, γ, and δ, to which, principally through the researches of Armstrong and Wynne (P., 1888, **4**, 105; 1889, **5**, 48; 1890, **6**, 128), the respective constitutions 2:8, 2:6, 2:5, and 2:7 have been assigned. Of these isomeric acids, those containing the sulphonic group in an α-position, namely, the 2:8 and the 2:5 acids, are simultaneously formed by sulphonation at low temperatures (15° to 100°), whilst those containing

the sulphonic group in a β-position, namely, the 2:6- and the 2:7-acids, are formed simultaneously by sulphonation at high temperatures (150° and above). The two homonucleal sulphonic acids, 2:1 and 2:4, have so far not been obtained by the sulphonation of β-naphthylamine, but are prepared by the action of ammonia on the corresponding sulphonic acids of β-naphthol.

Experimental.

The sulphonations were carried out under exactly comparable conditions, using a wide-mouthed, round-bottomed flask of 300 c.c. capacity closed by a rubber stopper, through which passed a glass tube terminating in a fine orifice in order to exclude the entrance of moisture during the operation. Ten grams of pure β-naphthylamine (twice distilled, m. p. 112°) were used for each sulphonation. This was coarsely powdered so as to pass a 30-mesh sieve, and added during ten minutes to the sulphuric acid contained in the flask, which was constantly shaken. The quantity of sulphuric acid used was four parts (40 grams) of 96 or 100 per cent. acid, or three parts (30 grams) of fuming sulphuric acid containing 20 per cent. of sulphur trioxide. As solution occurs, the temperature rises to nearly 60°, and if sulphonation below this temperature is desired, the flask must be cooled from time to time. As soon as solution was effected, the flask was stoppered and immersed in an oil-bath, the temperature of which was carefully regulated, where it was maintained at the requisite temperature for the time specified. The product was then mixed with 100 c.c. of water, and any lumps that were formed were broken down with a pestle. After half an hour, the precipitated sulphonic acid was collected on a Büchner funnel and washed with 75 c.c. of cold water, care being taken to keep the surface unbroken. The precipitate was then transferred to a porcelain dish, mixed to a fine paste with 50 c.c. of water, the mixture being heated to boiling and neutralised with 2*N*-sodium hydroxide, using phenolphthalein as indicator. The quantity of sodium hydroxide required for neutralisation indicates whether the sulphonation has proceeded correctly and whether the product has been washed free from sulphuric acid. If an incorrect quantity was used, the experiment was rejected. After cooling (and filtering to remove any β-naphthylamine if present), the solution of the sodium salt was evaporated to dryness on the water-bath, dried sharply at 100—105°, and weighed. In nearly every case the yield was about 96 per cent. of the theoretical.

For the separation and estimation of the isomeric acids, use was made, in the first place, of the insolubility of the sodium salt of

the 2:8-isomeride in 90—94 per cent. alcohol (Dahl's method). The sodium salts entering into solution consist of the 2:5-isomeride, together with any 2:6- and 2:7-isomerides that may be present in the sulphonation mixture. For the separation of the former from the two latter, a satisfactory method, based on the different solubility of the silver salts, was discovered. Whereas the silver salt of the 2:5-acid is fairly soluble in water, the silver salts of the 2:6- and 2:7-acids are very sparingly soluble and separate as white, silky precipitates on adding silver nitrate to even dilute solutions of the sodium salts.

In carrying out these separations, the dry sodium salt, obtained as above, was well powdered and a weighed quantity (15—16 grams) was extracted three times in succession with boiling 92—94 per cent. alcohol, using at each extraction about 90 grams of alcohol and boiling for fifteen to twenty minutes. The filtrates were united, the alcohol was distilled off, and the soluble and insoluble sodium salts were weighed after being dried. The latter consisted of practically pure 2:8-sulphonate, whilst the former was free from this salt, but contained the remaining isomerides. For the estimation of the 2:6- and 2:7-acids, 1 gram of the alcohol-soluble salt is dissolved in 20 c.c. of water in a small conical flask provided with a rubber stopper. Silver nitrate (5 to 10 c.c. of $N/5$-solution) is added, the mixture well shaken, and the precipitate collected after remaining for three or four minutes. The precipitated silver salt is washed with cold water and dissolved from the filter by ammonia. The solution is diluted to 100—200 c.c., boiled, and acidified with hydrochloric acid. The silver chloride is collected on a tared filter-paper, washed with boiling water, and weighed. From the weight of silver chloride obtained, the percentage of 2:6- and 2:7-acids is calculated, the difference being the 2:5-acid. The hot filtrate on cooling deposits the 2:6- and 2:7-acids in glistening plates. The accuracy of the method was demonstrated on mixtures containing known proportions of the respective isomerides.

The following numbers represent in nearly all cases the results of at least two concordant experiments.

Effect of Temperature.

In this series of experiments, sulphonation was effected with four parts of 96 per cent. sulphuric acid for five hours, whilst the temperature was raised from 40° to 120°.

No. of experiment.	Temperature.	Percentage of isomeric acids in product. 2 : 8.	2 : 5.	2 : 6 and 2 : 7.
1	40°	38	61·6	0·4
2	60	36	63·5	—
3	80	44	55·3	0·7
4	90	42	57·3	—
5	100	41	58·3	0·7
6	120	26	66·5	7·5

In experiments 2 and 4, the amount of 2:6- and 2:7-acids was not determined, but an average value was assumed in arriving at the percentage of the 2:5-acid.

It is seen that the maximum yield of the 2:8-acid is obtained at about 80° and diminishes with increase of temperature above this limit, whilst it is also somewhat less at lower temperatures.

Effect of Time.

The sulphonation was effected at 80°, using the same proportion of 96 per cent. sulphuric acid as in the previous series, but the time of reaction was varied from ten minutes to twenty-five hours.

No. of experiment.	Time, in hours.	Percentage of isomeric acids in product. 2 : 8.	2 : 5.	2 : 6 and 2 : 7.
7	1	42	57·3	0·7
8	2½	43	56·3	—
9	5	44	55·3	0·7
10	10	43	55·1	1·9
11	15	37	61·0	—
12	20	36	61·6	2·4
13	25	35	62·0	—

In experiments 8, 11, and 13, the amount of 2:6- and 2:7-acids was not determined, but an assumed value was used in arriving at the percentage of the 2:5-acid. The sulphonation is just completed within one hour, a shorter time than this leaving a little unaltered β-naphthylamine.

In order to ascertain the effect of reducing the time of reaction to the lowest possible limit, the following sulphonation was effected in about fifteen minutes at 50—60°. About 10 per cent. of the β-naphthylamine remained unsulphonated, and was collected after dissolving the acid in sodium carbonate solution.

No. of experiment.	Time and temperature.	Percentage of isomeric acids in product. 2 : 8.	2 : 5.	2 : 6 and 2 : 7.
14	15 minutes at 50–60°.	28	71·2	0·8

Effect of Strength of Sulphuric Acid.

In order to determine the effect of the concentration of the acid, sulphonations were conducted at varying temperatures with 92, 96 (results already given), and 100 per cent. sulphuric acid, and also with fuming sulphuric acid containing 20 per cent. of sulphur trioxide. With one exception, the time of reaction was fixed at five hours. In the experiment marked with an asterisk it was only ten to fifteen minutes. The following table gives the percentages of 2:8-acid found. When 92 per cent. sulphuric acid was employed, about 10 per cent. of β-naphthylamine escaped sulphonation.

Temperature of sulphonation.	Acid strength. 92 per cent. H_2SO_4.	96 per cent. H_2SO_4.	100 per cent. H_2SO_4.	20 per cent. SO_3.
20°	—	—	33	—
40°	—	38	39	38*
60°	—	36	38	—
80°	40°	44	40	46
90°	—	42	—	—
100°	—	41	23	—
120°	—	26	32	—

The percentage of 2:6- and 2:7-isomerides was only determined in the alcohol-soluble sodium salts obtained from the series of sulphonations made at 80°:

With 92 per cent. H_2SO_4 ..... 0·9 per cent. of 2 : 6- and 2 : 7-acids.
„ 96 „ H_2SO_4 ..... 0·7 „ „ „
„ 100 „ H_2SO_4 ..... 1·5 „ „ „
„ 20 „ SO_3 ..... 2·7 „ „ „

Conclusions from above Results.

It would appear from the results obtained that within temperatures ranging from 20° to 80° there is only a small variation in the proportion of the 2:8- to the 2:5-isomeride, which together constitute 97—99·5 per cent. of the entire sulphonation product.

The effect of variations in time is very similar; for periods between one hour and ten hours there is little difference in the proportion of the isomerides formed. Also within these limits of temperature and time the strength of the sulphuric acid appears to exert but little influence, with the exception that at 80° a small rise in the amount of the 2:6- and 2:7-isomerides is noticeable, with an increase in the concentration of sulphur trioxide.

Although within the limits of time and temperature mentioned the proportion of 2:8- and 2:5-acids does not greatly vary, the

lowest temperatures and shortest time of reaction seem to favour the production of the 2:5-acid.

Above the limits of time and temperature defined, a more marked variation becomes apparent, the time and temperature at which this change sets in being somewhat lowered as the concentration of acid is increased. In proportion as the temperature of 80° is exceeded or the sulphonation period (at 80°) is prolonged beyond ten hours, the percentage of the 2:8-acid falls, whilst that of the 2:5-acid rises. Simultaneously therewith there is an increased production of the 2:6- and 2:7-acids, the quantity of which reaches 7·5 per cent. with 96 per cent. sulphuric acid at 120°.

This curious result can only be explained in the following way:

The proportion of the 2:8-acid existent at any particular time and temperature may be regarded as a combination of two factors, namely, (*a*) the proportion of the 2:8- and 2:5-isomerides formed simultaneously in the first instance, and (*b*) the amount of subsequent conversion of the 2:8- into the 2:5-acid. Whilst in regard to the first factor low temperature and quick reaction would seem to favour the formation of the 2:5-acid, with regard to the second factor it would appear that the isomeric change of the 2:8- into the 2:5-acid only comes into evidence at temperatures above 80° and for periods of heating (at 80°) more than ten hours. In other words, it may be assumed that for temperatures below 80° the proportion of the 2:8- and 2:5-isomerides is a fixed one for a particular temperature, the sulphonic group entering simultaneously in the 5- and 8-positions. The proportion so fixed is fairly stable and can only be disturbed by heating to temperatures above 80°, by prolonged action of sulphuric acid, or by the use of a higher concentration of sulphur trioxide. The sulphonic group then commences to wander from the 8-position to the 5-position.

Experiments on Isomerisation.

In order to test the validity of the foregoing hypothesis, the behaviour of pure 2:1-, 2:8-, and 2:5-acids towards sulphuric acid was studied under the conditions existent during sulphonation.

Isomerisation of the 2:1-*Acid.*—It has been suggested that the first stage in the sulphonation of β-naphthylamine may be the entry of the sulphonic group in the 1-position, to be quickly followed by a transposition to the 5- and 8-positions. We have not been able in any instance to detect the presence of the 2:1-acid, even when the sulphonation had been conducted at the lowest possible temperature and in the shortest time.* If, therefore, the 2:1-acid is an

* Following a suggestion by Mr. G. Lodge, we have employed for the detection of the 2:1-acid the delicate reaction with bromine water in the

intermediate product, it must undergo isomerisation with great rapidity. In order to test this point, the following experiments were carried out.

A.—A quantity (17 grams) of the pure sodium salt of β-naphthylamine-1-sulphonic acid equivalent to 10 grams of β-naphthylamine was heated with 40 grams of sulphuric acid (96 per cent.) for five hours at 80°. Disappearance of the 2:1-acid only took place slowly. The product was worked up in the usual manner, the resultant dry sodium salt weighing 17 grams. On extraction with alcohol as usual, 46 per cent. of the 2:8-acid was obtained, whilst the portion soluble in alcohol consisted of 52·5 per cent. of the 2:5- and 1·5 per cent. of the 2:6- and 2:7-acids.

B.—Another experiment was performed under the same conditions, but with 100 per cent. sulphuric acid. The change of the 2:1-acid again occurred very slowly, and it was possible to detect it by the bromine test even after three hours' heating. After five hours the transformation was complete, and the product was then found to contain 40 per cent. of the 2:8-acid.

C.—In a third experiment, made with 96 per cent. sulphuric acid, the mixture was heated only for ten or fifteen minutes to 50—60°. In this case, 8 per cent. of β-naphthylamine was obtained, whilst the greater part of the product was unchanged 2:1-acid.

From the formation of β-naphthylamine in experiment *C*, and the production of the isomeric acids in experiments *A* and *B* in the same proportion as they are obtained by the direct sulphonation of β-naphthylamine, it may be inferred that the isomerisation is brought about by hydrolysis of the 2:1-acid to β-naphthylamine and subsequent resulphonation. In view of the considerable stability of the 2:1-acid under the conditions of sulphonation, it is clear that this acid cannot be an intermediate stage of the direct sulphonation. Hence in the latter, the sulphonic group must enter the second nucleus directly and not through intermediate formation of the homonucleal isomeride.

Isomerisation of the 2:8-Acid.—The pure 2:8-acid was heated with sulphuric acid (96 per cent.) at 80° for five hours. On working up the product as usual, it was found that 32 per cent. in one case and 27 per cent. in another had been converted into the 2:5-isomeride. The rate of this transformation under different

cold by which 1-bromo-β-naphthylamine is formed with the elimination of sulphuric acid. This reaction may also be used for the quantitative estimation of the 2:1-acid by weighing the sulphuric acid eliminated as barium sulphate. All other monosulphonic acids of β-naphthylamine give brominated acids without elimination of the sulphonic group (compare Vaubel, *Zeitsch. angew. Chem.*, 1900, **14**, 686).

conditions is shown in the following series of experiments, in which the pure sodium salt of the 2:8-acid (10 grams) was heated with sulphuric acid (80 grams) at varying temperatures and concentrations for a period of ten hours.

	Temperature.	2:8-Acid unconverted.	2:5-Acid formed (containing less than 1 per cent. of 2:6 and 2:7).
With 80 per cent. H_2SO_4	80°	78·5	21·5
	90	72·8	27·2
	100	70·7	29·3
	110	71·3	28·7
	120	69·8	30·2
With 90 per cent. H_2SO_4	90	63·7	36·3
	100	62·3	37·7
	110	57·2	42·8
	120	56·3	43·7

Isomerisation of the 2:5-*Acid.*—In a similar series of experiments, the pure 2:5-acid was subjected to the action of 96 per cent. sulphuric acid for five hours at 80°. When worked up as usual, the product gave a sodium salt completely soluble in alcohol and containing no 2:8-acid. It consisted almost entirely of unaltered 2:5-acid with a very small percentage of the 2:6- and 2:7-isomerides.

There is therefore no equilibrium established between the 2:8- and 2:5-acids in a sulphuric acid solution, for the isomeric change occurs in one direction only, namely, from 2:8 to 2:5.

Relative Rate of Hydrolysis of the Isomeric Sulphonic Acids.

Whilst the sulphonic group in β-naphthylamine-1-sulphonic acid is somewhat readily removed, the heteronucleal acids are more resistant, although no data are available as to the relative facility with which the different isomerides undergo hydrolysis. It appeared probable that in such differences might be found an explanation of the above facts.

With this object in view, 2 grams of the pure sodium salt of the 2:8-acid was heated with 20 grams of sulphuric acid (60 per cent.) in a small weighed flask on a sand-bath. The water was allowed to evaporate slowly, whilst from time to time samples were withdrawn and tested for β-naphthylamine by neutralisation with sodium hydroxide. No hydrolysis occurred until the temperature reached 145°. At this point, which was found to correspond with a concentration of 70 per cent. sulphuric acid, the undissolved sulphonic acid passed into solution, and at the same time β-naphthylamine was formed.

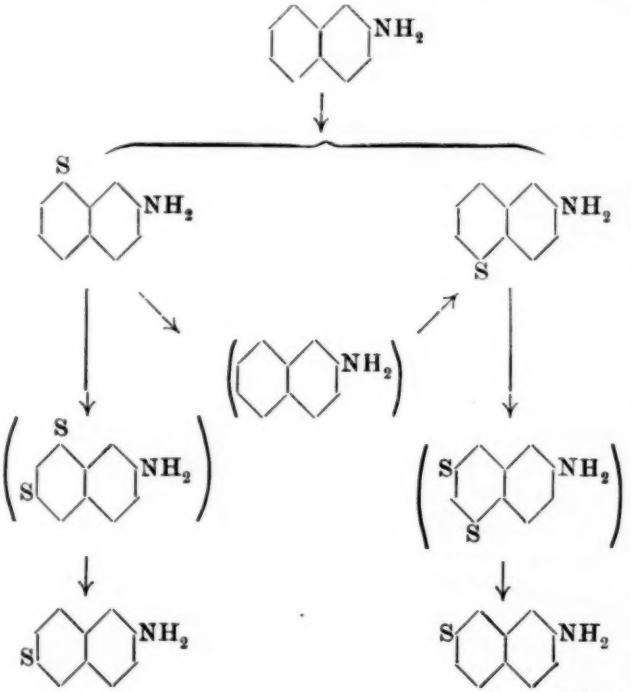
In a similar experiment with the 2:5-acid, solution and hydrolysis did not occur until a temperature of 160° was reached, corresponding with a concentration of 75 per cent. sulphuric acid.

With the 2:6- and 2:7-acids, no evidence of hydrolysis could be obtained even at 175°. The relative facility with which the isomeric acids undergo hydrolysis to β-naphthylamine may therefore be expressed thus:

$$2:1 > 2:8 > 2:5 > 2:6 \text{ and } 2:7.$$

It may therefore be concluded that the gradual conversion of the 2:8- into the 2:5-acid during long heating with sulphuric acid at temperatures of 80° to 120° is brought about by repeated hydrolysis of the 2:8-acid and resulphonation of the β-naphthylamine produced. At each resulphonation, about 40 per cent. of 2:8- and 60 per cent. of 2:5-acid is produced, the former of which is again hydrolysed to β-naphthylamine, and so on.

Simultaneously with the conversion of the 2:8-acid into the 2:5-acid, there also occurs to a less extent a transformation into the 2:6- and 2:7-acids. The last change, which is negligible below 100—110°, becomes considerable at temperatures above 120° (especially when sulphuric acid of high concentration is employed),



until at 150—160° the 2:6- and 2:7-isomerides constitute the main product of sulphonation. It appears probable that the formation of the latter acids is due to concurrent disulphonation and hydrolysis, in which sase the 2:6-acid would originate from the 2:8- and the 2:7-acid from the 2:5.

The entire mechanism of the sulphonation may probably therefore be expressed by the above scheme ($S=SO_3H$):

Copper and Silver Salts of the Isomeric Sulphonic Acids.

In seeking for a method of differentiating and estimating the isomeric acids, we have studied the behaviour of solutions of their sodium salts towards copper sulphate and silver nitrate. The results are given in the following table:

Acid.	$CuSO_4$.	$AgNO_3$.
2:8	Slowly deposits a reddish-orange precipitate.	Rather sparingly soluble precipitate.
2:5	Deep red solution, but no precipitate.	No precipitation in moderately concentrated solutions.
2:6	Sparingly soluble yellow precipitate.	Very insoluble, white, silky precipitate.
2:7	Sparingly soluble orange-yellow precipitate.	Similar, but yellower.

The silver salts of the four isomerides have been prepared in the solid state, and form nearly colourless, crystalline powders. On analysis, the following results were obtained: Found, 2:8, Ag=32·7; 2:5, Ag=32·8; 2:6, Ag=32·9; 2:7, Ag=33·0. Calc., Ag=32·73 per cent.

Determination of their solubilities in water at 15° gave the following results, the numbers indicating parts of water in which one part of the respective acid dissolves: 2:8, 300; 2:5, 70; 2:6, 4900; 2:7, 2800.

We desire to express our thanks to Messrs. Levinstein, Ltd., who have kindly supplied us with the materials required in this investigation.

DYESTUFFS RESEARCH LABORATORY,
MUNICIPAL SCHOOL OF TECHNOLOGY,
MANCHESTER. [*Received, November 12th*, 1917.]

VII.—*The Effect of Temperature and of Pressure on the Limits of Inflammability of Mixtures of Methane and Air.*

By Walter Mason and Richard Vernon Wheeler.

A "limit" mixture of an inflammable gas with air or oxygen can be defined as such that the heat evolved by the combustion of one "layer" of the mixture is sufficient, and only just sufficient, to raise to its ignition-temperature the layer adjacent, so that flame once started in such a mixture continues to be propagated progressively throughout, without the necessity for the continued presence of the source of heat that caused the inflammation.

The self-propagation of flame through the mixture is only possible when the speed of reaction between the combining gases is sufficient to overcome any loss of heat, by radiation, convection, and conduction, under the conditions of its combustion. The speed of reaction is dependent on the temperature that the portion of the mixture which is burning can impart to the portion that is about to burn.

It follows naturally, therefore, that the higher the initial temperature of the mixture the less is the propagation of flame dependent upon the heat generated by combustion, so that the effect of increasing the initial temperature of mixtures of methane and air should be to widen their limits of inflammability, lowering the lower and raising the upper limit.

The effect of pressure on the limits is not so easy to forecast; in point of fact, the results of experiments did not fulfil our anticipations. It will be best to leave discussion of the matter until the experiments have been described.

The Effect of Temperature.

The earliest systematic experiments on the effect of temperature on the limits of inflammability of gaseous mixtures seem to have been by Bunte and Roszkowski in 1890 (*J. Gasbeleuchtung*, 1890, **33**, 491, 524, 535, 553). The mixtures were ignited electrically in a spherical vessel of 35 c.c. capacity. Apart from the fact that it is impossible to judge accurately as to the propagation of flame in such a vessel, something must have been radically wrong with Bunte and Roszkowski's experimental arrangements, for they recorded no marked change in the limits for mixtures of methane

and air when the initial temperature of the mixtures was raised from 15° to 300°.

Taffanel (*Compt. rend.*, 1913, **157**, 593) examined the effect of increased temperature on the lower limit for mixtures of methane and air by passing an electric spark in the mixtures, after introducing them into a tube at the required temperature, and observing whether or no inflammation was propagated throughout the mixture. His results were as follow:

Initial temperature of mixture	20°	175°	237°	312°	555°	690°
Lower limit, methane in air, per cent.	5·80	5·25	4·75	4·30	3·40	3·00

Taffanel did not state the dimensions of his tube, the position of the point of ignition of the mixtures, or the direction of travel of the flames; but from his results, which, as will be seen later, closely correspond with our own, we conclude that a rather wide and short tube was used and that ignition was at the top, the flames being propagated vertically downwards.

Burrell and Robertson (United States Bureau of Mines, Technical Paper No. 121, 1916) repeated Taffanel's experiments, using a Hempel bulb of 100 c.c. capacity as the explosion vessel and igniting the mixtures near the top by an electric spark. The bulb was heated in an electric furnace, and whether or no flame had propagated throughout the mixture was judged by analysing the products of combustion. The results recorded were:

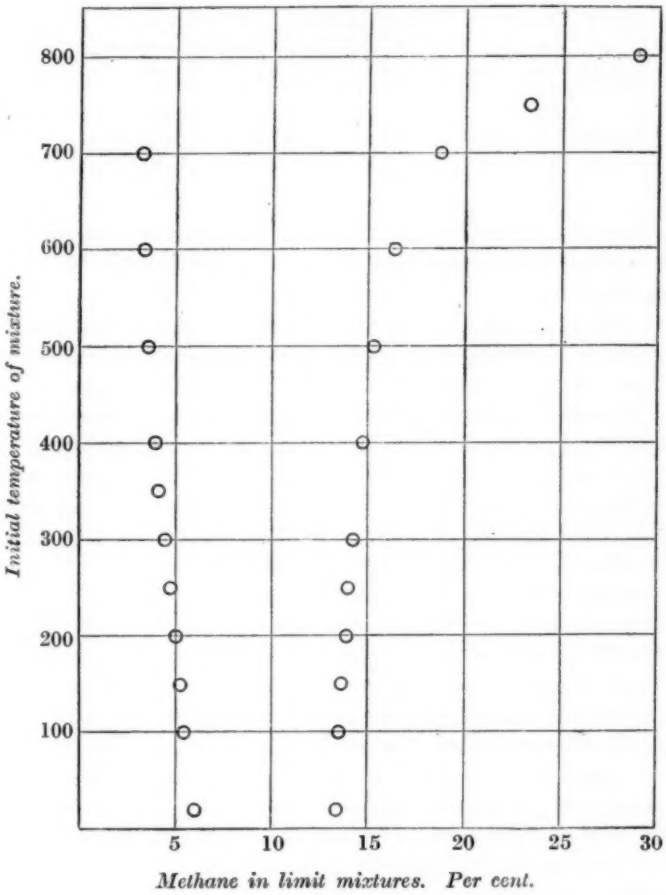
Initial temperature of mixture.	25°	200°	300°	400°	500°
Lower limit, methane in air, per cent.	5·46–5·56	4·98–5·15	4·75–4·88	4·47–4·55	3·75–4·00

Accurate observation of the propagation of flame in a vessel that is totally enclosed in an electric furnace presents some difficulty. It is not easy to judge, for example, of the extent of downward propagation of flame in a tube by an arrangement of mirrors, since the flame is viewed end-on; and analysis of the gases remaining after flame has passed, not altogether satisfactory as a means of judging whether flame has travelled or has just failed to travel throughout the vessel with lower-limit mixtures, gives quite misleading results with the upper-limit mixtures where much of the combustible gas remains unburnt or incompletely burnt.

For our experiments we have made use of the fact that the limits for upward propagation of flame are wider than for downward propagation (T., 1914, **105**, 2591) to aid in observing whether

or no flame travelled throughout the mixtures at different temperatures, in the manner described in the experimental portion of this paper. The criterion of inflammability adopted was self-propagation of flame downwards. The gaseous mixtures were stored over

FIG. 1.



a mixture of equal parts by volume of glycerol and water in glass gas-holders, whence they were introduced into the previously heated and evacuated explosion vessel; they were thus saturated with water vapour at the room temperature (20°). The results are given in the table that follows and diagrammatically in Fig. 1.

Initial temperature.	Downward propagation of flame in mixtures of methane and air. Methane, per cent.	
	Lower limit.	Upper limit.
20°	6·00	13·40
100	5·45	13·50
150	5·20	13·60
200	5·05	13·85
250	4·60	14·00
300	4·40	14·25
350	4·15	not determined.
400	4·00	14·70
500	3·65	15·35
600	3·35	16·40
700	3·25	18·75
750	—	23·60
800	—	29·00

The mixtures were allowed to remain during two seconds in the explosion vessel (which had been previously brought to the required temperature) before the passage of an electric spark to cause ignition. This length of time was sufficient to ensure that the gases attained the temperature of the enclosure (compare Burrell and Robertson, *loc. cit.*, p. 6), and at the same time, except perhaps at the highest temperatures, did not admit of appreciable combustion on the surface of the vessel before the spark was passed.

Consider first the lower limit. Progressive increase of the initial temperature causes a corresponding decrease in the amount of methane required in the air to enable self-propagation of flame to take place. Our determinations agree closely with Taffanel's, and therefore disprove Bunte and Roszkowski's results. With an initial temperature of 750°, a mixture containing 3·00 per cent. of methane ignited without being sparked (and flame was propagated throughout) as soon as it entered the explosion vessel, the rate of reaction on the surface of the explosion vessel at this temperature being sufficiently rapid to cause self-heating of the mixture. At 700° no ignition occurred with a 3·20 per cent. mixture by the walls of the vessel, nor was flame propagated throughout such a mixture when an electric spark was passed; for complete propagation of flame at this temperature the mixture had to contain 3·25 per cent. of methane. Under the conditions of these experiments, therefore, the ignition-temperature (that is, the temperature at which rapid self-heating takes place) of a 3 per cent. methane–air mixture can be regarded as between 700° and 750° (compare Taffanel, *loc. cit.*, p. 597).

Just as the lower limit is lowered by increasing the initial temperature, the upper limit is raised. The extent to which the limit is raised increases regularly with the initial temperature of

the mixture until 600° is exceeded, after which there is a considerable rise in the rate of increase (see Fig. 1). This is probably due to reaction between methane and oxygen on the surface of the explosion vessel being sufficiently rapid with high concentrations of methane at temperatures above 600° to alter the constitution of the mixture during the two seconds that elapse between its introduction into the heated explosion vessel and the passing of the spark. We know that with excess of methane in air, carbon monoxide and hydrogen (both of which have very high upper limits of inflammability) persist in the products of combustion, and it may be that the early production of these gases is the cause of the abnormal raising of the upper limit of inflammability of mixtures of methane and air at temperatures greater than 600°. That combustion without flame takes place to an appreciable extent above 600° under the conditions of the experiments is shown by the fact that at 700° no ignition could be obtained (with a mixture containing 18·70 per cent. of methane) if the mixture were left in the explosion vessel longer than five seconds before sparking, whilst at 750° an interval of only 1·5 seconds sufficed to render a mixture containing 23·50 per cent. of methane uninflammable. In each of these instances we can assume that the mixtures became uninflammable by deprivation of oxygen consequent on its burning the methane. If, therefore, the formation of carbon monoxide and hydrogen by combustion of methane is the cause of the abnormal raising of the upper limit at these high temperatures, the effect is transitory. Hydrogen would be produced also by thermal decomposition of methane, but the reaction is very slow at temperatures below 900°. In any event, it is clear that the results obtained at temperatures above 600° do not properly represent the upper limits for self-propagation of flame in mixtures of *methane* and air.

It may be mentioned that in no instance did ignition of, and propagation of flame in, a high-limit mixture take place through contact with the heated walls of the explosion vessel. At 800°, for example, a spark had to be passed in order to cause flame to travel through the mixture (containing 28·70 per cent. of methane).

The Effect of Pressure.

The effect of initial pressure above atmospheric on the limits of inflammability of mixtures of hydrogen, carbon monoxide, and methane, respectively, with air has been studied by Terres and Plenz (*J. Gasbeleuchtung*, 1914, **57**, 990, 1001, 1016, 1025). The explosion vessel used was an iron cylinder 37 cm. long and 8 cm. in diameter. Ignition was by an electric spark at a point 4 cm.

from the top of the cylinder and on its vertical axis. The criterion of inflammability was, therefore, self-propagation of flame downwards. Whether or no flame had passed throughout the mixture was judged by analysing the products of combustion.

For methane (firedamp from Kissarmas, Transylvania, containing 99·1 per cent. of methane), Terres and Plenz obtained the results shown in the tables that follow.

Lower Limit.

Methane in mixture. Per cent.	Initial pressure. Mm. mercury.	Methane burned. Per cent.
6·00	760	99
6·00	1520	22
6·00	2280	11
6·00	3800	7
6·15	1520	99
6·15	2280	26
6·15	3800	13
6·23	1520	100
6·23	2280	100
6·23	3040	31
6·23	3800	17
6·41	3800	100
6·41	4560	98
6·41	5320	50
6·41	6080	30
6·41	7600	12
6·44	5320	100
6·44	6080	98
6·44	6840	52
6·58	7600	100

Upper Limit.

Methane in mixture. Per cent.	Initial pressure required for propagation of flame. Mm. mercury.
12·98	760
13·35	2280
13·65	4560
13·98	6840

With upper-limit mixtures, according to Terres and Plenz, either the mixture did not burn at all under the conditions of their experiments or flame travelled throughout. No partial propagation of flame took place as with the lower-limit mixtures. Their experiments can be summarised in the statement that an increase of the initial pressure of the mixtures to 10 atmospheres

raised the lower limit (downward propagation of flame) from 6·0 to 6·5 per cent., and also raised the upper limit from 13·0 to 14·0 per cent.

Burrell and Robertson (*loc. cit.*) also studied the effect of pressure on the limits of inflammability of mixtures of methane and air, using the same apparatus as for their work on the effect of temperature. Their experiments were mainly at pressures less than atmospheric, but they recorded that "increasing the initial pressure up to 5 atmospheres had no effect in changing the low limit of complete propagation" (p. 10). At reduced pressures, they found that the limits were narrowed, until at pressures between 250 and 300 mm. of mercury it was impossible, under the conditions of their experiments, to obtain self-propagation of flame in any mixture of methane and air.

Our experiments at reduced pressures have been made with initial temperatures of 20°, 250°, and 500°. The same apparatus was used as for the experiments with different initial temperatures at atmospheric pressure. The results are shown diagrammatically in Fig. 2.

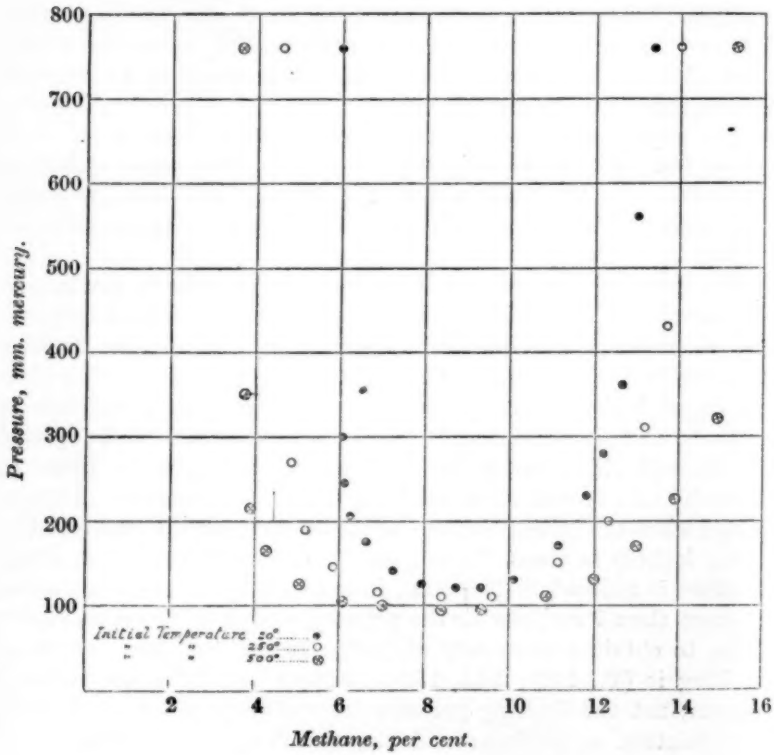
The fact that Burrell and Robertson were unable to obtain self-propagation of flame in any mixture at pressures less than 300 mm. (at atmospheric temperature), whereas we found the limiting pressure to be 120 mm., is explicable on the assumption that their means of ignition was inadequate. For example, a mixture of methane and air containing 9·5 per cent. of methane can be ignited at atmospheric pressure by the secondary discharge from an "8-inch" *X*-ray coil at a spark-gap of 1 mm. between platinum points when the current broken in the primary circuit (the trembler being locked) is about 0·5 ampere; but when the pressure of the mixture is reduced to 100 mm., it is necessary to break a current of more than 7 amperes in the primary circuit of the same coil in order to obtain a secondary discharge at a 1 mm. gap capable of igniting it (T., 1917, **111**, 130). Burrell and Robertson's results express, not the limiting pressure for *self-propagation of flame* in any mixture of methane and air, but the limiting pressure for *ignition* by a secondary discharge of the particular intensity employed by them.

Examination of Fig. 2 shows that at atmospheric temperature the mixtures of methane and air in which flame is propagated (downwards) most readily, as evinced by their having the lowest limiting pressure, contain between 8·75 and 9·40 per cent. of methane.

The same conclusion can be drawn from the experiments by Burgess and Wheeler on "limit" mixtures of methane, oxygen,

and nitrogen (T., 1914, **105**, 2596). Those experiments showed that by the gradual substitution of nitrogen for the oxygen in air the limits were narrowed until, when the "atmosphere" contained only 13·45 per cent. of oxygen, they lay between 6·50 per cent. (lower) and 6·70 per cent. (upper) of methane. From the partial pressures of the gases, the percentages of methane in the atmospheric air contained in these limit mixtures can be calculated, the presence of the excess of nitrogen and of methane (above that

FIG. 2.



required for complete combustion by the oxygen) being regarded as equivalent to a reduction of pressure. This calculation gives 9·2 per cent. of methane in air as the mixture that propagates flame most readily.

The mixtures of methane and air most readily ignited by a secondary discharge, or by the break-flash ("momentary arc") produced at the point of fracture of a metallic electric circuit (continuous current), contain between 8·0 and 8·6 per cent. of

methane, whilst the mixtures in which the "uniform movement" of propagation of flame is most rapid contain between 9·5 and 10·0 per cent. of methane (T., 1914, **105**, 2607).

The range of mixtures over which propagation of flame occurs most readily thus lies mid-way between the range over which ignition (by electrical means) is easiest and the range over which the flames are fastest. It might be argued from this that ease of propagation of flame in a series of mixtures of methane and air is dependent about equally on the ease of ignition of the mixtures and on the ratio $T-t/t-\theta$ (see T., 1917, **111**, 1044). It must be remembered, however, that the ignitibility of the mixtures, as shown by the intensity of the secondary discharge or the primary break-flash required to ignite them, is not necessarily a measure of their ignitibility by heated gases during the propagation of flame.

The effect of raising the initial temperature of the mixtures is to widen the dilution limits at all pressures, and the limiting pressure for the self-propagation of flame in any mixture is lowered, though not to a great extent. A point in these experiments that should be noted is the small effect on the limits produced by reducing the initial pressures by as much as half an atmosphere; the effect does not begin to be marked until the pressure is reduced below 300 mm.

For experiments with initial pressures greater than atmospheric, we have used a tube of stout glass into which the previously prepared mixtures could be forced through a condensing syringe in the manner described in the experimental portion of this paper. The criterion of inflammability was, as before, propagation of flame downwards. The results were as follow:

Initial pressure. Mm. mercury.	Lower limit. Methane, per cent.	Upper limit. Methane, per cent.
760	6·00	13·00
1250	6·05	13·15
2100	not determined.	13·35
2900	6·20	13·60
3350	6·25	not determined.
3750	not determined.	13·80
4650	6·40	14·05

We thus confirm Terres and Plenz's results. For the lower-limit mixtures, our values agree closely with theirs, but we obtained a greater raising of the upper limit by increasing the pressure than they recorded. This, we think, is due to Terres and Plenz not having used a sufficiently powerful source of ignition, for they have stated that the mixtures either did not ignite at all or flame travelled throughout them. This is contrary to our ex-

perience, for we obtained many mixtures at high pressures in which flame travelled only part of the way down the tube. Mixtures of methane and air containing more than 11 per cent. of methane require a secondary discharge of considerable intensity to ignite them, and the intensity required increases rapidly with increased methane content. Thus, a mixture of methane and air, at atmospheric pressure, containing 12 per cent. of methane, can be ignited by the secondary discharge from an "8-inch" *X*-ray coil across a spark-gap of 3 mm. when a current of 7·5 amperes is broken in the primary circuit (the trembler being locked), whereas a mixture containing 13 per cent. of methane requires 15 amperes, and one that contains 14 per cent. 32 amperes. On the other hand, an increase of the pressure (above atmospheric pressure) of any of the mixtures renders it capable of being ignited by a discharge of slightly less intensity (T., 1917, **111**, 411).

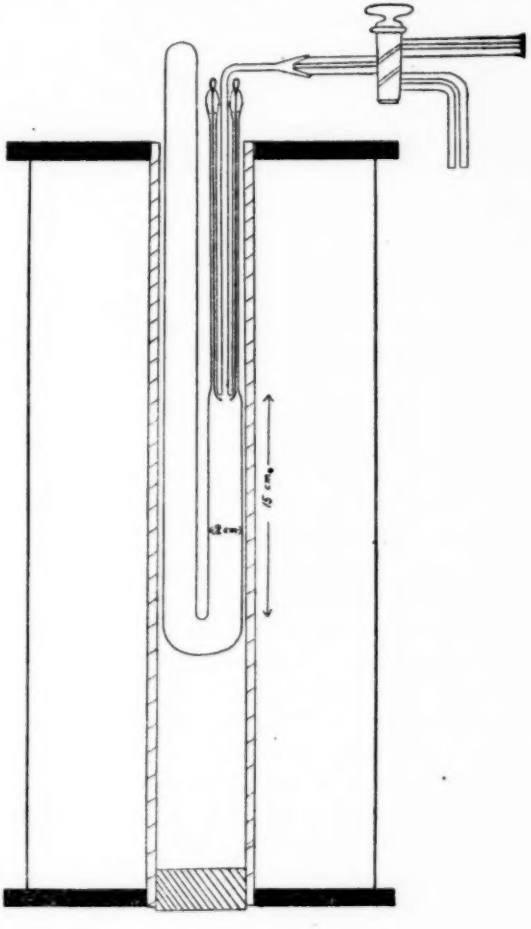
It is easy to see, therefore, by the manner in which they expressed their results, how Terres and Plenz confused the inability of their secondary discharge to ignite some of their mixtures with incapability of the mixtures to propagate flame. They recorded, for example, that a mixture containing 13·65 per cent. of methane did not propagate flame—did not burn at all—when the initial pressure was 6 atmospheres; on raising the pressure to 7 atmospheres (when the mixture would be rendered more readily ignitible), flame was propagated throughout.

Leaving differences in degree aside, however, we are in agreement with Terres and Plenz in observing a raising of both the lower and the upper limit with increased initial pressure (above atmospheric), and we find the results difficult to explain. From the law of mass action, we anticipated that increased pressure, if it had any appreciable effect after atmospheric pressure had been passed, would widen the limits on both sides. If the widening of the upper limit be explained by mass action, what is the reason for the narrowing of the lower limit?

According to the kinetic theory, loss of heat from gases by conduction and radiation is independent of the pressure. When attempting to put this deduction from the kinetic theory to experimental proof, however, Kundt and Warburg (*J. de Physique*, 1876, **5**, 118) found that unless the pressure of the gas was low, the loss of heat due to conduction was masked by that arising from convection currents. It may be, therefore, as Terres and Plenz have suggested, that the loss of heat from a gas at high pressure is due to a greater extent to convection than to conduction, and increases with the pressure. According to this explanation, the upper limit should also be narrowed, and when hydrogen

or carbon monoxide is the combustible gas this is so. What must be regarded as the abnormal behaviour of mixtures of methane and air under pressure at the upper limit requires further study.

FIG. 3.



EXPERIMENTAL.

The apparatus used for determining the limits of inflammability at different temperatures and at pressures less than atmospheric is shown in Fig. 3. It consisted essentially of a U-tube of transparent quartz, the limbs of which were close together, fixed vertically in a tube furnace which could be heated electrically. One limb of the U-tube was 15 cm. long and had a capillary

extension which was fitted, by means of a ground joint, with a glass three-way tap, of the form shown in the diagram, to make connexion with either a vacuum pump or a gasholder and mercury manometer. The other, longer, limb (35 cm.) was sealed at the top, which projected above the level of the furnace. The electrodes for igniting the mixtures were platinum wires led into the quartz tube, immediately below the capillary extension, through capillary side-tubes, the upper ends of which were closed by plugs of glass ground in, through which the platinum wires were sealed. The spark-gap was 4 mm.

Since the limits for upward (or horizontal) propagation of flame are wider than for downward propagation, a mixture which on ignition enabled flame to travel just the full length of the shorter limb of the U-tube easily carried flame up the longer limb, and its appearance could be observed in the portion of the tube above the furnace, either directly or, as was found more convenient during experiments at low pressures, in a mirror inclined at an angle of 45° fixed above the top of the tube and enclosed in a darkened box.

Ignition was caused by a short series of sparks from an "8-inch" *X*-ray coil, with a current of 15 amperes in the primary circuit. The intensity of this discharge with a 4 mm. spark-gap was well in excess of the minimum required for the least easily ignitible mixtures, whilst the length of the tube was sufficient to ensure that the initial impetus imparted to the flames by the source of ignition had died away before the bottom was reached.

For the experiments at high pressures, a tube of thick glass 18 cm. long and of 2 cm. internal diameter was employed, fixed vertically. The tube was provided at the top with a high-pressure three-way tap of capillary bore, to make connexion with either a vacuum pump or a condensing syringe in communication with a gas-holder containing the mixture to be experimented with. A high-pressure tap at the bottom of the tube communicated with a Bourdon pressure gauge. The electrodes were platinum wires sealed into the glass at the top of the tube, the spark-gap being 4 mm. A secondary discharge of the same intensity as for the experiments in the quartz tube was used to ignite the mixtures. The lower third of the tube was covered on the outside with black paper, in which a horizontal slit 2 mm. wide was cut at a distance of 15 cm. from the point of ignition; flame was judged to have travelled throughout the tube if it was observed to pass this slit.

For the experiments at different temperatures, the method of procedure was to obtain two mixtures, differing by 0·10 per cent. of methane, the one enabling flame to appear in the longer limb

of the quartz U-tube, whilst with the other no flame appeared. The mean percentage of methane in the two mixtures was taken as the limiting percentage. For the experiments at different pressures, two pressures were obtained for a given mixture, differing by 10 mm. of mercury at pressures below atmospheric or by 50 mm. at higher pressures, such that at one pressure flame appeared in the prescribed manner, whilst at the other it did not. The mean pressure was taken as the limiting pressure for the particular mixture under the conditions of the experiment.

The methane was obtained from a natural source of firedamp and purified by liquefaction. The mixtures with air (free from carbon dioxide) were prepared in glass gas-holders over glycerol and water, and were analysed before use.

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VIII.—*The Relation of Position Isomerism to Optical Activity. Part XI. The Menthyl Alkyl Esters of Terephthalic Acid and its Nitro-derivatives.*

By Julius Berend Cohen and Hannah Smith de Pennington.

In a former paper (T., 1916, **109**, 222), a series of menthyl alkyl esters of phthalic and 3-nitrophthalic acid were prepared and examined, with the following results: whilst the free carboxyl group in the acid menthyl ester raises the molecular rotation nearly 100° ($[M]_D^{20}$ −332°) above that of menthyl benzoate ($[M]_D^{20}$ −239°), the average rotation of seven menthyl alkyl esters ($[M]_D^{20}$ −243°) did not differ greatly from that of menthyl benzoate—in other words, the proximity of the carboxyl group raises the rotation, whilst that of the ester group produces little effect.

In the case of the parallel series of terephthalic esters, which is the subject of the present paper, the main difference in structure lies in the separation of the two carboxyl groups. One might therefore expect that, like the menthyl alkyl esters of phthalic acid, the alkyl ester group would have little or no influence on the active group, and that the molecular rotations of these substances would be of the same order as that of menthyl benzoate. This anticipation has been realised, the average molecular rotation of seven menthyl alkyl esters of terephthalic acid being $[M]_D^{20}$ −254°. In this case, the average rotation is somewhat higher

than that for the corresponding menthyl alkyl phthalates ($[M]_D^{20}$ −243°). In spite of numerous attempts, it was found impossible to obtain the acid menthyl ester in the crystalline state, but the amorphous product prepared by the semi-hydrolysis of dimenthyl terephthalate gave the correct numbers on analysis, and may be regarded as fairly pure. Its rotation was $[M]_D^{18}$ −259·2°.

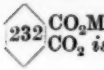
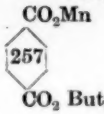
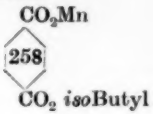
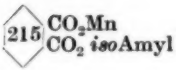
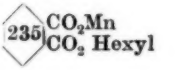
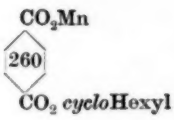
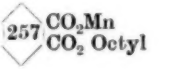
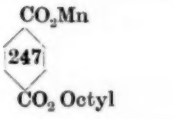
It therefore appears that the carboxyl, like the nitro-group, whilst raising the rotation of the active group in the ortho-position, has little or no effect in the para-position.

	$[M]_D^{20}$.		$[M]_D^{20}$.
o-Nitromenthyl benzoate ...	−381°	*p*-Nitromenthyl benzoate ...	−237°
Menthyl hydrogen phthalate	−332	Menthyl hydrogen terephthalate	−259

Menthyl benzoate $[M]_D^{20}$ −239°.

It is somewhat remarkable that whilst the free carboxyl group in the para-position differs little in its effect from that of the ester groups in the same position, both carboxyl and ester group give a higher value than the unsubstituted menthyl benzoate or its *p*-nitro-derivative. The following table gives the parallel series of esters of phthalic and terephthalic acid, molecular rotations, $[M]_D^{20}$ (lævo), being given in round figures within the hexagon (Mn = menthyl).

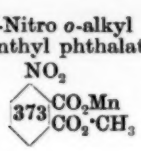
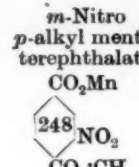
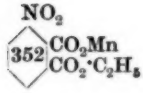
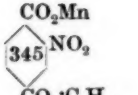
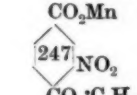
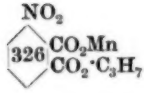
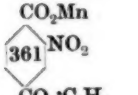
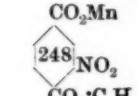
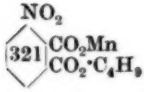
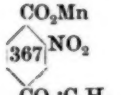
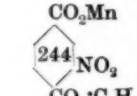
Phthalic esters.	Terephthalic esters.
444 CO_2Mn, CO_2Mn	CO_2Mn, 526, CO_2Mn
332 CO_2Mn, CO_2H	CO_2Mn, 259, CO_2H
268 CO_2Mn, CO_2Me	CO_2Mn, 246, CO_2Me
254 CO_2Mn, CO_2Et	CO_2Mn, 255, CO_2Et
242 CO_2Mn, CO_2Pr	CO_2Mn, 255, CO_2Pr

Phthalic esters.	Terephthalic esters.	
		
	—	
		
		

In addition to those points to which attention has been directed, it will be further observed that whilst the rotation of the menthyl alkyl esters of phthalic acid decrease steadily to the *iso*amyl compound and then rise, so that the two end members have the highest rotations, the opposite effect is seen in the case of the terephthalic esters, the two end members possessing the lowest rotations. Further, the molecular rotation of menthyl terephthalate is much higher than that of the corresponding phthalic ester, and about double that of the acid menthyl terephthalate.

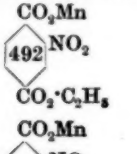
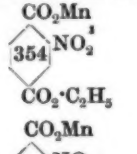
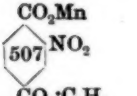
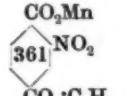
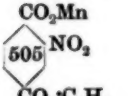
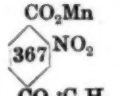
If the van't Hoff theory of optical superposition held, and assuming that the two menthyl ester groups in dimenthyl terephthalate to be so far separated as not to influence one another's rotations, the half value ($-263°$) should correspond approximately with that of menthyl benzoate ($-239°$). Unless the hydrogen atom in the para-position lowers the rotation, which does not seem very probable, it would appear that the ester groups in dimenthyl terephthalate influence one another to the extent of raising the rotation about 12°, whilst the average increase for the other members is 15°.

Turning now to the nitro-derivatives, it has been already pointed out that the proximity of the nitro-group to the menthyl ester group greatly increases the rotation, whilst that in the meta- and ortho-position does not. Much the same result has been observed in the two series of menthyl alkyl nitroterephthalates.

o-Nitro *o*-alkyl menthyl phthalate.	*o*-Nitro *p*-alkyl menthyl terephthalate.	*m*-Nitro *p*-alkyl menthyl terephthalate.
	—	
		
		
		

It will be seen from the above table that the proximity of the nitro-group to the active group raises the rotation, being of the same order, although rather lower than that of menthyl *o*-nitrobenzoate ([M] $-381°$) and the corresponding nitrophthalates ([M] $-343°$ mean). Here again the curious anomaly is observable that whereas in the nitrophthalic esters the rotation falls with the larger alkyl group, the reverse occurs with the corresponding nitroterephthalic esters. On the other hand, the nitro-group in the meta-position with respect to the active group reduces the average value ([M] $-247°$) to the order of the un-nitrated ester ([M] $-254°$), that is to say, produces little or no effect.

Another curious anomaly to which attention must be directed is the enhanced rotation of the nitromenthyl esters in benzene solution.

$[M]_D^{20}$. In benzene solution.	$[M]_D^{20}$. In the fused state.
	
	
	

The difference might be ascribed to association, but a determination of the molecular weight of dimenthyl nitroterephthalate (which in benzene has a rotation of $[M]_D^{20} - 781°$) by the cryoscopic method in benzene gave a normal result:

0·0851 in 8·79 benzene gave $\Delta^t = -0·1°$. M.W. = 483.

$C_{28}H_{41}O_6N$ requires M.W. = 487.

We are at a loss to account for these abnormal rotations in solution. It suggested, however, a possible explanation of the high values of the *m*-nitro *o*-alkyl menthyl phthalates, all of which being solid at the ordinary temperature were examined in benzene solutions (*loc. cit.*, p. 225); but a comparison of the rotation of *m*-nitro *o*-methyl menthyl phthalate with that of the homogeneous liquid at 100° showed that the solvent had practically no effect. The numbers are:

$[M]_D^{20}$ in benzene.	$[M]_D^{100}$ fused.
−446°	−439°

The following is a brief summary of the results:

(1) The mutual effect of two menthyl ester groups in the para-position is considerably greater than that of the same groups in the ortho-position.

(2) This is true to a less extent of the alkyl ester group.

(3) The carboxyl group in the para-position has much the same effect as the alkyl ester groups.

(4) The nitro-group in the ortho-position with respect to the active group raises the rotation by about 100°; that in the meta-position has little effect.

(5) The esters with the nitro-group in the ortho-position with respect to the active group exhibit enhanced rotation in benzene solution.

There appears no reason, therefore, to modify the generalisation defined in the former paper (T., 1914, **105**, 1895), namely, that the element or group lying nearest to the active group produces the greatest effect.

Experimental.

The Menthyl Alkyl Esters of Terephthalic Acid.

The method employed in the preparation of these esters may be illustrated in the case of menthyl ethyl terephthalate.

In a small distilling flask fitted with an air condenser was placed a mixture of 12 grams of dry, powdered terephthalic acid and 30 grams of phosphorus pentachloride. The substances were well mixed and warmed gently until the reaction began, being after-

wards heated on the water-bath until solution was obtained. The phosphoryl chloride was removed by distillation on the water-bath under diminished pressure in a current of dry air. The residue was extracted with benzene and filtered to separate excess of phosphorus pentachloride, which is not dissolved. The solvent was removed by heating on the water-bath, and finally under diminished pressure. The yield of acid chloride was 22 grams. To the acid chloride, 20 grams (twice the theoretical amount) of absolute ethyl alcohol was added, and cooled until the first reaction had moderated, when the mixture was heated on the water-bath for half an hour.

The contents of the flask were then dissolved in ether and the ethereal solution shaken up with small quantities of dilute sodium carbonate solution to remove any free acid, after which it was dehydrated over anhydrous sodium sulphate and distilled, first at the ordinary pressure to remove ether, and then under diminished pressure. The yield of diethyl terephthalate was 11 grams (b. p. 148°/2 mm.; m. p. 36—40°).

It was then half hydrolysed as follows: A mixture of 11 grams of the diethyl ester in 14 c.c. of ethyl alcohol and 3 grams of potassium hydroxide in 3 c.c. of water and 14 c.c. of ethyl alcohol was well shaken, when the contents solidified. After heating for half an hour on the water-bath, a little water was added, and the unchanged diethyl ester separated by extracting with small quantities of ether. After removing any residual ether by heating, the solution was cooled and acidified with hydrochloric acid. The solid which separated was collected and crystallised from benzene, in which terephthalic acid is very sparingly soluble.

In this way, 4 grams of pure acid ethyl ester, melting at 168—170°, were obtained. The ester was heated with a large excess of thionyl chloride (8 grams) under reflux on the water-bath until dissolved, any insoluble impurity being removed by filtration. The excess of thionyl chloride was distilled on the water-bath under diminished pressure, and the residue (4 grams), which crystallised on cooling, melted at 27°. The calculated quantity of menthol (3 grams) was added, and the whole heated gradually in an oil-bath to 110—120° for an hour or more, until the evolution of hydrogen chloride ceased. The excess of menthol was then removed by distillation in a current of steam and the residue extracted with ether. The ethereal solution, after shaking with sodium carbonate solution, was dehydrated over calcium chloride and decolorised with charcoal, and then distilled, first on the water-bath and then with the flame and under diminished pressure.

The excess of alcohol used in the preparation of esters of the

higher alcohols was removed by distillation under diminished pressure.

The following table gives the melting and boiling points of the dialkyl esters and the alkyl acid esters.

Dialkyl terephthalate.	M. p.	B. p.	Alkyl hydrogen terephthalate.		M. p.
Dimethyl	140°	—	Methyl, hydrogen		About 230° Indefinite.
Diethyl	36—40	142/2 mm.	Ethyl	,,	168—170
Dipropyl.....	Liquid	158/4 mm.	Propyl	,,	127—129
Di-*n*-butyl	Liquid	180/4 mm.	Butyl	,,	122—124
Di*iso*butyl	40—43	180/6 mm.	*iso*Butyl	,,	151—154
Di*cyclo*hexyl	75—80	—	*cyclo*Hexyl	,,	160—162
Dioctyl	—	decomposed	Octyl	,,	82— 84

The menthyl alkyl esters obtained by the method described above are viscid liquids with a faint yellow colour which could not be removed by charcoal. The rotations were determined with the pure substances in a 0·302-dcm. tube at 20° and 100°.

Alkyl menthyl terephthalate.	$a_D^{20°}$.	D_4^{20}.	$[a]_D^{20°}$.	$[M]_D^{20°}$.	$a_D^{100°}$.	$D_4^{100°}$.	$[a]_D^{100°}$.	$[M]_D^{100°}$.
Methyl	24·66	1·054	77·49	246·3	23·11	1·000	76·52	243·3
Ethyl I.....	24·45	1·060	76·38	253·6	21·78	0·998	72·28	240·0
,, II	24·42	1·050	77·45	257·0	21·76	0·991	72·58	240·9
Propyl	23·20	1·041	73·79	255·4	20·72	0·9845	69·69	241·2
n-Butyl	22·39	1·037	71·48	257·3	19·90	0·9848	66·91	240·9
*iso*Butyl	23·30	1·044	73·91	266·1	20·86	0·988	69·92	238·2
*cyclo*Hexyl I...	20·90	1·034	67·06	258·9	18·63	1·009	61·14	236·0
,, II...	21·42	1·038	68·33	263·7	19·09	1·004	62·92	242·9
Octyl I	17·84	0·999	59·13	246·0	15·96	0·947	55·82	232·2
,, II	17·91	0·999	59·36	246·9	16·03	0·945	56·16	233·6

The following are the analytical results:

Alkyl menthyl ester.	Formula.	Found. Carbon.	Found. Hydrogen.	Calculated. Carbon.	Calculated. Hydrogen.
Methyl menthyl	$C_{19}H_{36}O_4$	71·60	8·20	71·69	8·18
Ethyl menthyl ...	$C_{20}H_{38}O_4$	72·16	8·48	72·30	8·44
*cyclo*Hexyl menthyl	$C_{24}H_{34}O_4$	74·66	8·78	74·68	8·81
Octyl menthyl ...	$C_{26}H_{40}O_4$	74·99	9·66	75·01	9·62

Neutral and Acid Menthyl Esters of Terephthalic Acid.

The neutral ester was obtained in the usual way from the acid chloride, the excess of menthol being subsequently removed by steam distillation. It crystallised from hot alcohol in needle-shaped crystals melting at 77—78°.

I. 0·5208 in 25 c.c. benzene in a 2-dcm. tube at 13° gave α −4·91; hence $[a]_D^{13}$ −117·9; $[M]_D^{13}$ −521·1.

At 100° in a 0·302-dcm. tube; D^{100} 0·979.

α_D^{100} – 30·22; $[\alpha]_D^{100}$ – 102·3; $[M]_D^{100}$ – 451·7.

II. 0·5210 in 25 c.c. benzene in a 2-dcm. tube at 12·5° gave α – 4·96; hence $[\alpha]_D^{12·5}$ – 119; $[M]_D^{12·5}$ – 525·9.

At 100° in a 0·302-dcm. tube; D^{100} 0·978.

α_D^{100} – 30·3; $[\alpha]_D^{100}$ – 102·6; $[M]_D^{100}$ – 453·5.

0·1830 gave 0·5100 CO_2 and 0·1569 H_2O. C = 76·00; H = 9·53.

$C_{28}H_{42}O_4$ requires C = 76·02; H = 9·50 per cent.

The acid ester was prepared by the semi-hydrolysis of the neutral ester as follows: An alcoholic solution containing 1·3 grams of potassium hydroxide was added to 10 grams of dimenthyl terephthalate, and the mixture heated on the water-bath for two hours. The product was poured into water, and the unchanged neutral ester and menthol extracted with ether. After removing the ether, hydrochloric acid was carefully added to the slightly warm solution, when an oil separated which was dissolved in a small quantity of benzene (in which terephthalic acid dissolves sparingly). The benzene solution was dehydrated with anhydrous sodium sulphate, and the benzene removed first on the water-bath and finally under diminished pressure. The residue consisted of a colourless, resin-like substance which did not crystallise:

0·1805 gave 0·4723 CO_2 and 0·1265 H_2O. C = 71·33; H = 7·78.

$C_{18}H_{24}O_4$ requires C = 71·06; H = 7·89 per cent.

0·5160 in 25 c.c. benzene in a 2-dcm. tube gave α_D^{18} – 3·52; hence $[\alpha]_D^{18}$ 85·11; $[M]_D^{18}$ 259·2.

Neutral and Acid Menthyl Esters of Nitroterephthalic Acid.

The nitroterephthalic acid was prepared by the method described by Burkhardt (*Ber.*, 1877, **10**, 145). The dimenthyl ester was obtained in the usual way by treating the acid chloride (formed by the action of phosphorus pentachloride on the acid) with the calculated amount of menthol and purifying in the manner already described. After recrystallisation from alcohol, it was obtained in colourless needles melting at 88°:

0·1532 gave 0·3873 CO_2 and 0·1168 H_2O. C = 68·93; H = 8·47.

$C_{28}H_{41}O_6N$ requires C = 68·98; H = 8·42 per cent.

0·5084 in 25 c.c. benzene in a 2-dcm. tube gave α_D^{15} – 6·53; hence $[\alpha]_D^{15}$ – 160·5; $[M]_D^{15}$ – 781·2.

At 100° in a 0·302-dcm. tube the pure ester gave α_D^{100} – 36·26. $[\alpha]_D^{100}$ – 116·0; $[M]_D^{100}$ – 564·8.

The acid ester was prepared by the semi-hydrolysis of the neutral

ester with the calculated quantity of potassium hydroxide in methyl alcohol in the manner already described in the previous section. After removing unchanged neutral ester, the acid ester was precipitated by the careful addition of concentrated hydrochloric acid. The solid acid ester was collected and crystallised from aqueous alcohol, when it melted at 75°:

0·1550 gave 0·3515 CO_2 and 0·0924 H_2O. C = 61·84; H = 6·62.
$C_{18}H_{23}O_6N$ requires C = 61·9; H = 6·59 per cent.

A second preparation gave the same result.

On reconverting the acid ester into the dimenthyl ester by treating with excess of thionyl chloride and heating the resulting acid chloride with menthol, the product had the same rotation as that found for the ester obtained by the previous method of preparation.

o-*Nitro* p-*Alkyl Terephthalic Esters.*

The esters were prepared as follows: The acid menthyl ester was heated with excess of thionyl chloride on the water-bath until a clear solution was obtained, the excess being removed under diminished pressure. The acid chloride was then heated under reflux with an excess of alcohol on the water-bath for about an hour until the reaction was complete. The product was poured into water, the ethereal extract being shaken with small quantities of dilute sodium carbonate solution and dehydrated over calcium chloride, with the addition of animal charcoal. After removing the ether, the nitroalkyl menthyl esters were obtained as viscid liquids, with the exception of the methyl ester, which crystallised in needle-shaped crystals melting at 78—79°.

The rotations were determined in the fused state in a 0·302-dcm. tube at 20° and 100°, and also in benzene solution in a 2-dcm. tube.

o-Nitro p-alkyl menthyl terephthalate.	In the fused state. a_D^{20}.	D_D^{20}.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
Methyl	—	—	—	—
Ethyl	−31·56	1·410	−91·58	−345·2
Propyl I	31·09	1·110	92·74	352·6
,, II	31·20	1·126	91·77	358·8
n-Butyl I	29·64	1·098	90·48	366·5
,, II	30·04	1·099	90·51	366·8

o-Nitro p-alkyl menthyl terephthalate.	In the fused state. a_D^{100}.	D_4^{100}.	$[\alpha]_D^{100}$.	$[M]_D^{100}$.
Methyl	−30·50	1·093	−92·41	−335·5
Ethyl	28·52	1·08	85·45	322·2
Propyl I	27·79	1·055	87·22	341·0
,, II	27·92	1·063	87·02	340·2
n-Butyl I	26·57	1·043	84·33	341·6
,, II	26·62	1·040	84·74	343·3

o-Nitro *p*-alkyl menthyl terephthalate.	In benzene solution. Gram in 25 c.c. benzene.	a_D^{18}.	$[a]_D^{18}$.	$[M]_D^{18}$.
Methyl I	0·4996	−5·65	−141·4	513·0
,, II	0·3665	4·16	141·7	515·0
Ethyl	0·5100	5·45	130·5	491·8
Propyl	0·6032	6·21	129·7	507·2
Butyl	0·5052	5·04	124·7	505·2

On analysis, the following results were obtained:

Alkyl menthyl ester.	Formula.	Found. Carbon.	Found. Hydrogen.	Calculated. Carbon.	Calculated. Hydrogen.
Methyl	$C_{19}H_{23}O_6N$	62·81	6·85	62·81	6·89
Ethyl	$C_{20}H_{27}O_6N$	63·49	7·26	63·66	7·16
Butyl	$C_{22}H_{31}O_6N$	65·11	7·70	65·18	7·65

m-Nitro p-*Alkyl Menthyl Terephthalic Esters.*

The esters were obtained by the semi-hydrolysis of the neutral alkyl esters. The acid alkyl ester thus obtained was converted into the acid chloride, which was then heated with menthol and purified in the usual way.

The following table gives the melting and boiling points of the dialkyl and *m*-nitro *p*-alkyl esters, all of which were crystallised from benzene.

	m-Nitro *p*-alkyl menthyl ester. M. p.	*m*-Nitro *p*-alkyl acid ester. M. p.
Methyl	72—74°	174—176°
Ethyl	48	146—148
Propyl	B. p. 192/6 mm.	135—137
Butyl	B. p. 215/6 mm.	132—134

The rotations were determined in the fused state in a 0·302-dcm. tube at 20° and 100°.

m-Nitro *p*-alkylmenthyl ester.	a_D^{20}.	D_4^{20}.	$[a]_D^{20}$.	$[M]_D^{20}$.	a_D^{100}.	D_4^{100}.	$[a]_D^{100}$.	$[M]_D^{100}$.
Methyl	23·38	1·133	68·31	248·0	20·58	1·096	62·19	—
Ethyl I	22·31	1·127	65·55	247·1	19·55	1·074	60·67	—
,, II	22·29	1·130	65·31	246·2	19·48	1·074	60·06	—
Propyl	21·25	1·130	62·25	248·4	18·80	1·060	58·73	—
Butyl	20·66	1·136	60·23	244·0	18·36	1·057	57·53	—

The following results were obtained on analysis:

Nitro alkyl menthyl ester.	Formula.	Found. Carbon.	Found. Hydrogen.	Calculated. Carbon.	Calculated. Hydrogen.
Ethyl	$C_{20}H_{27}O_6N$	63·60	7·20	63·66	7·16
Butyl	$C_{22}H_{31}O_6N$	65·21	7·60	65·18	7·65

THE UNIVERSITY,
LEEDS.

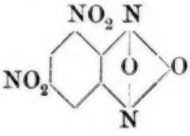
[*Received, December 12th,* 1917.]

IX.—*Nitro-derivatives of* iso*Oxadiazole Oxides and of* iso*Oxadiazoles.*

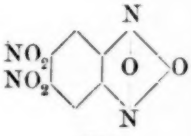
By Arthur G. Green and Frederick Maurice Rowe.

In a previous communication (T., 1913, **103**, 2025) we have directed attention to the so-called "nitro-*o*-dinitrosobenzene and dinitro-*o*-dinitrosobenzene" obtained by Drost (*Annalen*, 1899, **307**, 54) by the nitration of benz*iso*oxadiazole oxide (then termed *o*-dinitrosobenzene).

The dinitro-compound (I) is of special interest, because it



(I.)

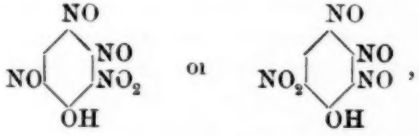


(II.)

possesses acidic properties, reacting, for example, with potassium hydrogen carbonate to form the potassium salt, $C_6HN_4O_6K,\frac{1}{2}H_2O$ (Drost).

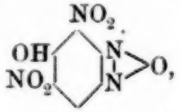
Zincke and Schwarz (*Annalen*, 1899, **307**, 32) consider that the metal in this potassium salt is probably directly attached to carbon and that it is the hydrogen atom between the two nitro-groups which is replaced, for the isomeric dinitro-compound (II) possesses no acidic properties.

As an alternative, Zincke and Schwarz suggest the possibility that the salt may be a derivative of the isomeric compound,



which is reconverted into the original oxadiazole oxide on treating the salt with acid. The latter hypothesis does not appear to us to afford a satisfactory explanation in view of the improbability that oxygen should wander with such facility from the nitro-group to the carbon nucleus and back again, merely under the influence of weak alkalis or acids. If the acidic properties are to be explained by the presence of a hydroxyl group, it would seem more probable that the latter is formed in the nitration of the benz*iso*-

oxadiazole oxide, the product of which might possibly be a dinitrohydroxybenz*iso*oxadiazole,

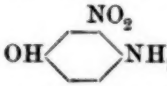


rather than dinitrobenz*iso*oxadiazole oxide.

In order to test this possibility, the pure compound was reduced with titanous chloride. If a hydroxyl group is present, 18 atoms of hydrogen will be required for complete reduction, whereas if there is no hydroxyl group present, 20 atoms of hydrogen will be needed.

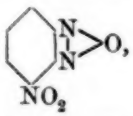
Experiment showed that 20 atoms of hydrogen are required, thus proving the compound to be a true dinitrobenz*iso*oxadiazole oxide. We are therefore reduced to the conclusion that we have here, in fact, an example of hydrogen in the benzene ring possessed of acidic properties.

An attempt was made to obtain a hydroxy-derivative of benz*iso*oxadiazole oxide by the oxidation of nitro-*p*-aminophenol,



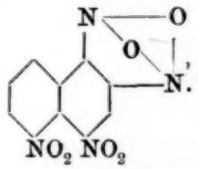
with sodium hypochlorite, with the object of preparing its nitro-derivatives. It was found, however, that oxidation of nitro-*p*-aminophenol under all conditions resulted in the disruption of the ring, accompanied by the formation of chloropicrin, and nothing else could be isolated. The hydroxyl group must therefore be added to the list of substituents already given (T., 1917, **111**, 613) which, when occupying the para-position with respect to the amino-group in a substituted *o*-nitroamine, render the ring unstable to oxidation with hypochlorite.

In view of the interest attaching to dinitrobenz*iso*oxadiazole oxide, it appeared desirable to investigate also the dinitro-derivative of benz*iso*oxadiazole, of which only the mononitro-derivative,



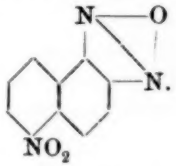
has been prepared by Drost (*Annalen*, 1899, **307**, 69). All our attempts to prepare a dinitro-derivative, however, failed, whether benz*iso*oxadiazole or nitrobenz*iso*oxadiazole was employed, and whether nitration was effected in the cold or at higher temperatures, with one or with more than one molecular proportion of nitric acid.

Finally, we have prepared and examined the previously unknown nitro-derivatives of naphth*iso*oxadiazole oxide and of naphth*iso*-oxadiazole itself. Nitration of naphth*iso*oxadiazole oxide in sulphuric acid solution with three, four, or five molecular proportions of nitric acid, either in the cold or at 50°, gave rise to a single product. On diminishing the quantity of nitric acid to two, one and a-half, or one molecular proportion, the same product was also obtained, although in admixture with unaltered naphth*iso*-oxadiazole oxide. It crystallises in yellow needles melting at 215°, and on analysis with titanous chloride proved to be a dinitro-compound. No trace of a mononitro-compound was obtainable. The dinitronaphth*iso*oxadiazole oxide is very resistant to oxidation, but 3-nitrophthalic acid in sufficient amount for identification was obtained by prolonged boiling with chromic acid and acetic acid. This proves that a nitro-group is situated in each ring, one being in position 5 or 8 and the other in position 4 or 3. Most probably the substance has the constitution



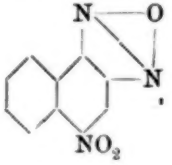
Owing to the destructive decomposition exerted by dilute alkalis, it was not found possible to convert the compound into the corresponding dinitronaphthaquinonedioxime or dinitronaphth*iso*-oxadiazole.

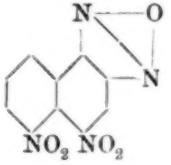
Naphth*iso*oxadiazole differs considerably from naphth*iso*oxadiazole oxide in its behaviour on nitration. When nitrated in sulphuric acid solution with one and a-half molecular proportions of nitric acid, it is completely converted into a product which crystallises in needles melting at 143°. Analysis by titanous chloride showed this product to be a mononitronaphth*iso*oxadiazole. Oxidation with chromic acid and acetic acid produced 3-nitrophthalic acid, showing that the nitro-group is in position 5 or 8. The compound most probably has the constitution



It differs from the nitro-derivatives which follow in that it is not affected by alkalis and does not react with aniline. When the

quantity of nitric acid is increased to 3, 4, or 5, or even 10, molecular proportions, a mixture of two compounds is always obtained, the separation of which may be readily effected by means of alcohol. The amount of the more readily soluble product decreases with increase of the quantity of nitric acid used, and with 10 molecular proportions of nitric acid it is only formed in traces. It crystallises in yellow leaflets melting at 147°. The less readily soluble portion, which constitutes the main product of reaction, crystallises in long, yellow needles melting at 196°. On analysis with titanous chloride, the former product proved to be a mononitronaphth*iso*oxadiazole, the latter a dinitro*iso*oxadiazole. Oxidation of the dinitro-compound produced 3-nitrophthalic acid, whilst from the mononitro-compound phthalic acid was obtained. Hence the nitro-groups are in positions 5 or 8 and 4 or 3 in the dinitro-compound, and in positions 4 or 3 in the mononitro-compound. Their constitution may most probably be represented thus:





The mononitro-compound differs from the previously described isomeride in reacting with alkalis and with aniline. In this respect it is similar to the dinitro-compound. It appears, therefore, that reactivity with alkalis and with aniline is conditioned by the presence of a nitro-group in the same ring as the furazan group. On further nitration, both mononitro-derivatives give rise to the above dinitro-compound.

Experimental.

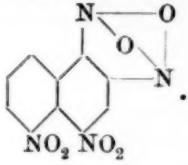
3:5-*Dinitrobenz*iso*oxadiazole Oxide* (*Dinitrobenzfuroxan*) (I).

This was prepared as described by Drost (*Annalen*, 1899, **307**, 54), by the nitration of benz*iso*oxadiazole oxide in sulphuric acid solution. It crystallised from acetic acid in large, yellow needles melting at 172°.

Titration with Titanous Chloride.—0·01 required 29·8 c.c. $TiCl_3$ (1 c.c. = 0·001655 grams Fe).

Calculated as $C_6H_2(NO)_2(NO_2)_2 = 99·5$ per cent., that is, 20H required for reduction.

4(or 3):5(or 8)-*Dinitronaphth*isoo*xadiazole Oxide* (*Dinitronaphthafuroxan*), *probably*



Ten grams of naphth*iso*oxadiazole oxide (T., 1917, **111**, 616) dissolved in 100 c.c. of concentrated sulphuric acid were nitrated by the addition of a mixture of 9 c.c. of nitric acid (95 per cent.) and 30 c.c. of concentrated sulphuric acid. The mixture was cooled at first, and then warmed to 50° and poured on ice. The product, when crystallised from glacial acetic acid or nitric acid, formed bunches of small, prismatic needles melting at 215°.

Titration with Titanous Chloride.—0·0105 required 23·6 c.c. $TiCl_3$ (1 c.c. = 0·001801 gram Fe).

Calculated as $C_{10}H_4(NO)_2(NO_2)_2 = 99·7$ per cent., that is, 20H required for reduction.

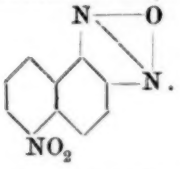
0·131 gave 22·5 N_2 at 16° and 762 mm. N = 20·14.

$C_{12}H_4O_6N_4$ requires N = 20·29 per cent.

Dinitronaphth*iso*oxadiazole oxide, when treated with potassium hydrogen carbonate in the manner described by Drost for the preparation of the potassium salt of dinitrobenz*iso*oxadiazole oxide, does not form a salt. It is, however, sensitive to alkalis, and dissolves with decomposition in boiling sodium carbonate or dilute sodium hydroxide solution, giving a reddish-brown solution with the evolution of ammonia and formation of nitrite. If, however, a little dilute sodium hydroxide is added to an aqueous suspension of the finely divided substance and the mixture cautiously warmed to 30—40°, solution occurs, and after some time a red precipitate separates. This product, which is apparently a salt, crystallises from water in fine, red leaflets. On gently warming the dry product, it decomposes with slight detonation. On acidifying its aqueous solution, a reddish-brown precipitate of impure dinitronaphth*iso*oxadiazole oxide is obtained. When warmed with aniline, dinitronaphth*iso*oxadiazole oxide behaves in an analogous manner to dinitrobenz*iso*oxadiazole oxide. It dissolves with a red colour, and, on the addition of alcohol an anilide separates in reddish-brown needles, which melt and decompose at 166°. This anilide is soluble in alkalis with a red colour, showing that reduction to the dioxime takes place simultaneously with the introduction of aniline into the nucleus.

In endeavouring to ascertain the position of the nitro-groups in dinitronaphth*iso*oxadiazole oxide, various methods of oxidation were tried. The substance is not affected by boiling with dilute or fuming nitric acid, and only by prolonged boiling with chromic and acetic acids was a small quantity of 3-nitrophthalic acid obtained. This crystallised in yellow prisms melting at 218°, and gave the anhydride melting at 163°.

5(or 8)-*Nitronaphth*isoo*xadiazole* (*Nitronaphthafurazan*),



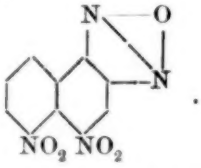
A solution of 10 grams of naphth*iso*oxadiazole in 100 c.c. of concentrated sulphuric acid was nitrated in the cold by adding a mixture of 3·6 c.c. of nitric acid (95 per cent.) and 15 c.c. of concentrated sulphuric acid. The product crystallised from nitric acid in almost colourless, silky needles melting at 143°. It is not affected by boiling with aqueous alkalis or alkaline sodium hypochlorite. It does not react with aniline.

Titration with Titanous Chloride.—0·0112 required 20·4 c.c. $TiCl_3$ (1 c.c. = 0·001708 gram Fe).

Calculated as $C_{10}H_5(N_2O)\cdot NO_2 = 99·6$ per cent., that is, 12H required for reduction.

Prolonged boiling with chromic and acetic acids converted this nitronaphth*iso*oxadiazole into 3-nitrophthalic acid, melting at 218°, and forming the anhydride melting at 163°.

4(or 3):5(or 8)-*Dinitronaphth*isoo*xadiazole* (*Dinitronaphthafurazan*),



A solution of 10 grams of naphth*iso*oxadiazole in 100 c.c. of concentrated sulphuric acid was treated with a mixture of 9·5 c.c. of nitric acid (95 per cent.) and 25 c.c. of concentrated sulphuric acid. The mixture was cooled at first and then warmed to 40°. The product crystallised from alcohol in long, yellow needles melting at 196°.

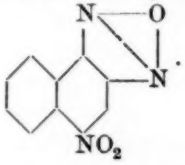
The same substance is obtained by further nitration of either of the two mononitronaphth*iso*oxadiazoles.

Titration with Titanous Chloride.—0·01 required 22·5 c.c. $TiCl_3$ (1 c.c. = 0·001712 gram Fe).

Calculated as $C_{10}H_4(N_2O)(NO_2)_2 = 99·4$ per cent., that is, 18H required for reduction.

*Dinitronaphth*isoo*xadiazole* dissolves in boiling dilute alkalis with decomposition. On the addition of a few drops of sodium hydroxide to a finely divided aqueous suspension and gently warming, a yellowish-brown solution is obtained, from which a brown, flocculent precipitate separates on keeping. This precipitate, when decomposed by acids, does not yield unaltered dinitronaphth*iso*oxadiazole. Dinitronaphth*iso*oxadiazole dissolves in aniline, on warming, with a reddish-brown colour. On the addition of alcohol, an anilide separates in long, reddish-brown needles melting at 98° and soluble in alkalis. Prolonged boiling with chromic and acetic acids converts the dinitronaphth*iso*oxadiazole into 3-nitrophthalic acid melting at 218°, and forming the anhydride melting at 163°.

4(or 3)-*Nitronaphth*isoo*xadiazole* (*Nitronaphthafurazan*),



On concentrating the mother liquors from which dinitronaphth*iso*oxadiazole has separated, a second crop of crystals is obtained. After twice recrystallising from alcohol, the product forms yellow leaflets melting at 147°. No method was found by which naphth*iso*oxadiazole could be completely converted into this compound.

Titration with Titanous Chloride.—0·0102 required 17·7 c.c. $TiCl_3$ (1 c.c. = 0·001801 gram Fe).

Calculated as $C_{10}H_5(N_2O)\cdot NO_2 = 99·9$ per cent., that is, 12H required for reduction.

4-Nitronaphth*iso*oxadiazole dissolves in boiling dilute alkalis with decomposition. On the addition of a few drops of sodium hydroxide to a finely divided aqueous suspension of the compound and gently warming, it dissolves with an orange-red colour, and a brown, flocculent precipitate separates on keeping. This precipitate is decomposed by acids, but does not yield unaltered nitronaphth*iso*oxadiazole. Nitronaphth*iso*oxadiazole dissolves in aniline on warming, with a reddish-brown colour. On the addition of alcohol, an anilide crystallising in red needles melting at 94° and

soluble in alkalis is obtained. Prolonged boiling with chromic and acetic acids converts this nitronaphth*iso*oxadiazole into phthalic acid, from which the anhydride melting at 128° is obtained.

In conclusion, we desire to express our thanks to Miss Eva Hibbert, who has kindly carried out the titrations of these nitro-compounds with titanous chloride.

DYESTUFF RESEARCH LABORATORY,
MUNICIPAL SCHOOL OF TECHNOLOGY,
MANCHESTER. [*Received, December 18th*, 1917.]

X.—*The Mercury Ammonia Compounds. Part. I.*

By MURIEL CATHERINE CANNING HOLMES.

A LARGE number of solid products of the action of aqueous and dry ammonia on mercury salts, either in the presence or absence of the corresponding salts of ammonium, have been described as distinct chemical compounds, but as the solids are in some cases non-crystalline precipitates, and the only evidence of their being chemical compounds is the approximate correspondence of the analyses with simple chemical formulæ, it is not improbable that some of these so-called compounds are solid solutions, the compositions of which vary with the conditions of precipitation, or even mixtures of two distinct phases. Franklin (*Amer. Chem. J.*, 1912, **47**, 361. See also *J. Amer. Chem. Soc.*, 1905, **27**, 835; 1907, **29**, 35; and *Zeitsch. anorg. Chem.*, 1905, **46**, 1), in an excellent summary of the extensive literature on this group of compounds, has emphasised the worthlessness of the evidence on which some of the products obtained have been characterised as chemical individuals. Four modern investigations of Gaudechon (*Ann. Chim. Phys.*, 1911, [viii], **22**, 145), Strömholm (*Zeitsch. anorg. Chem.*, 1908, **57**, 72), Widman (*Zeitsch. anorg. Chem.*, 1910, **68**, 1), and François (*Compt. rend.*, 1900, **130**, 332, 1022), to which reference will have to be made later, have, however, furnished results which were shown to be consistent with the phase rule, and in certain cases with the mass law.

The mercuriammonium compounds can be grouped under the three following classes:

I. The additive compounds of mercury salts and ammonia, of which fusible precipitate, $HgCl_2,2NH_3$, is the best known example.

II. The ammonolysed * compounds, in which one or other of the ammonia residues NH_2, NH, or N take the place of acid radicles in a mercury salt. Infusible precipitate, $ClHgNH_2$, is the simplest representative of this class.

III. The compounds which are both hydrolysed and ammonolysed. For example, the chloride of Millon's base

$$H_2N{\cdot}Hg{\cdot}O{\cdot}HgCl$$

or $HO{\cdot}Hg{\cdot}NH{\cdot}HgCl$.

It should here be mentioned that Rammelsberg (*J. pr. Chem.*, 1888, [ii], **38**, 563), Pesci (*Gazzetta*, 1889, **19**, 509; 1890, **20**, 485), and Gaudechon (*loc. cit.*) advocate the formulation of all three classes of substances as molecular compounds of dimercuriammonium, $ClHg_2N$, with different molecular proportions of water, ammonia, ammonium salts, and mercuric salts. However, Hofmann and Marburg (*Annalen*, 1899, **305**, 191; *Zeitsch. anorg. Chem.*, 1899, **23**, 126), and Franklin (*loc. cit.*) have pointed out that this unusual method of formulation cannot be adopted in the case of the mercury alkyl- and aryl-amines, although these must, in the absence of any evidence to the contrary, be regarded as constituted similarly to the corresponding mercuriammonium compounds. Furthermore, the same authors have shown, in the opinion of the writer convincingly, that Rammelsberg's dimercuriammonium theory is supported neither by analogy nor by any single fact which cannot be as satisfactorily explained by the older and more natural view of the structure of these substances.

The Additive Compounds of Mercuric Chloride and Ammonia.

Mercuric chloride unites with twelve molecular proportions of ammonia when it is treated with liquid ammonia, and at the same time ammonolysis takes place in accordance with the equation (Franklin, *loc. cit.*) $HgCl_2,12NH_3 = ClHgNH_2 + NH_4Cl + 10NH_3$.

The ammonium chloride produced dissolves in the liquid ammonia. It is probable that the change is reversible, and that in the presence of a saturated solution of ammonium chloride in liquid ammonia the ammine would be stable.

By the action of gaseous ammonia on mercuric chloride, fusible precipitate, $HgCl_2,2NH_3$, is formed; but this compound can be obtained as well-defined crystals by dissolving infusible precipitate or the chloride of Millon's base in a hot saturated solution of ammonium chloride and cooling the filtered solution. In this

* The term ammonolyse was introduced by Franklin. Its meaning corresponds with that of hydrolyse.

case, it has been shown by Gaudechon (*loc. cit.*) that the actions are reversible, in accordance with the equations

$$ClHg{\cdot}O{\cdot}HgNH_2 + NH_4Cl \rightleftharpoons 2ClHgNH_2 + H_2O,$$
$$ClHgNH_2 + NH_4Cl \rightleftharpoons HgCl_2,2NH_3.$$

The product obtained by Kane (*Ann. Chim. Phys.*, 1839, [ii], **72**, 215, 337) by heating mercuric chloride in dry ammonia, or by volatilising a mixture of mercuric oxide and ammonium chloride, and supposed by him to be $HgCl_2,NH_3$, is, according to Pesci (*Gazzetta*, 1890, **20**, 485) and Dammer ("Handbuch der Anorg. Chemie," II, 2, 803), probably a mixture.

It is therefore unlikely that any compound of mercuric chloride and ammonia containing a less proportion of ammonia than fusible precipitate has been prepared. In order to test if such a substance is capable of existence, dry ammonia was passed into an ethereal solution of mercuric chloride, the current of gas being stopped before all the mercuric chloride had been precipitated. The flocculent precipitate was washed with ether, left in a vacuum desiccator for several hours, and then analysed.* The analysis furnished the following numbers:

Found: Hg = 69·34; Cl = 24·30; NH_3 = 5·98.
$HgCl_2,NH_3$ requires Hg = 69·52; Cl = 24·58; NH_3 = 5·89 per cent.

This analysis proved that a lower ammine of mercuric chloride must exist, but it did not show that the compound was $HgCl_2,NH_3$, and, as a matter of fact, it will be shown later that the precipitate was almost certainly a mixture.

When the ethereal solution of mercuric chloride was saturated

* As the mercuriammonium compounds lose their ammonia only after prolonged boiling with concentrated alkali, and as the chlorine ion cannot be precipitated completely in the presence of a mercuric salt by silver nitrate, a special method of analysis had to be employed.

To estimate the mercury and ammonium, the salt to be analysed was dissolved in dilute hydrochloric acid: the mercury was precipitated as sulphide with hydrogen sulphide, and the precipitate collected, dried, and weighed in a Gooch crucible. The filtrate and washings were boiled to remove hydrogen sulphide. Sodium hydroxide was then added to the cooled solution, and the ammonia distilled off into a standard solution of acid.

To estimate the chlorine, another weighed portion of the salt was dissolved in dilute sulphuric acid, the mercury in the solution precipitated by hydrogen sulphide, and the sulphine removed by filtration. The hydrogen sulphide in the filtrate was then removed as completely as possible in a vacuum, the small quantity which remained being precipitated with copper sulphate in slight excess. The copper sulphide was filtered off and the chlorine determined in the filtrate by precipitation with silver nitrate.

with ammonia, the composition of the precipitate was approximately that of fusible precipitate, $HgCl_2,2NH_3$.

An attempt was next made to prepare the lowest ammine, namely, that which is stable in the presence of the solid mercuric chloride, by shaking the finely divided fusible precipitate, prepared as above, with a saturated ethereal solution of mercuric chloride. The analysis furnished results in agreement with the formula

$$HgCl_{1\cdot783}\ (NH_2)_{0\cdot217}\ (NH_3)_{0\cdot5581}.$$

The product must therefore have been partly ammonolysed during the washing with ether.

As the analysis appeared to indicate that it would be difficult to obtain a pure substance by the above method of preparation, another mode of preparing the substance, which it was thought might furnish it in a crystalline form, was tried. The experiments with ether had demonstrated that the compound it was desired to prepare was stable in the presence of a saturated solution of mercuric chloride in ether. It ought therefore to be stable in a saturated aqueous solution of mercuric chloride provided that ammonium chloride in sufficient quantity to prevent ammonolysis is dissolved in the water. From such a solution, therefore, an attempt was made to prepare the crystalline ammine.

Infusible precipitate was digested at 100° with solutions of mercuric chloride of different concentrations in an approximately concentrated solution of ammonium chloride, the solution filtered while hot from the undissolved precipitate, and allowed to cool slowly. Well-defined crystals began to separate out when the temperature had fallen almost to that of the laboratory, and gradually increased in amount for several hours. The crystals were rapidly separated from the mother liquor by means of the pump, washed twice with alcohol and twice with ether, left in the vacuum desiccator for several hours, and then analysed. The results, which are recorded in the following table, show that a compound, $3HgCl_2,2NH_3$, undoubtedly exists, and that it is improbable that there is a compound, stable at the ordinary temperature, intermediate in composition between this and fusible precipitate, $HgCl_2,2NH_3$.

In the top row of the table is given the composition of the liquid phase in grams of mercuric chloride in 100 grams of water containing about 42 grams of ammonium chloride, and in the next three rows are the percentages of mercury, ammonia, and chlorine in the solid phase.

Per cent. of	130 grams.	130 grams.	130 grams.	120 grams.
Hg	70·89	70·92	70·78	70·88
NH_3	4·066	4·022	3·98	4·086
Cl.....	—	25·01	25·01	—
Compound separated	$3HgCl_2,2NH_3$	$3HgCl_2,2NH_3$	$3HgCl_2,2NH_3$	$3HgCl_2,2NH_3$

Per cent. of	110 grams.	100 grams.	95 grams.	65 grams.
Hg	70·81	65·46	65·20	64·20
NH_3	3·998	10·70	10·66	11·48
Cl.....	—	—	—	—
Compound separated	$3HgCl_2,2NH_3$	$HgCl_2,2NH_3$	$HgCl_2,2NH_3$	$HgCl_2,2NH_3$

$3HgCl_2,2NH_3$ requires Hg = 70·84; NH_3 = 4·01; Cl = 25·15.
$HgCl_2,2NH_3$ requires Hg = 65·57; NH_3 = 11·13; Cl = 23·13 per cent.

Strömholm claims to have established the existence of a compound of the formula $HgCl_2,H_2NHgCl$, and Gaudechon of the compound $HgCl_2(Hg{:}N{\cdot}HgCl)_2$; but that the work on these compounds needs to be repeated is shown by the following quotation from Franklin's monograph on the mercuriammonium compounds.

"Strömholm was not sure of the existence of a chemical individual of the formula $Hg_5N_2Cl_4$. Gaudechon, on the contrary, obtained results pointing sharply to the formation of this compound, and asserted his belief that no compounds intermediate in composition between $Hg_5N_2Cl_4$ and the normal salt exist; that is, Gaudechon does not accept the existence of a compound of the formula $NH_2HgCl{\cdot}HgCl_2$."

I have therefore repeated Strömholm's work, and have obtained results which confirm his conclusions.

A dilute solution of ammonium chloride was nearly saturated with mercuric chloride. It was then heated at 100° for one or two hours with infusible precipitate, filtered, and left to cool. The precipitate obtained was in the form of a fine, white powder which, after washing and drying, was much more loose and bulky than the other mercuriammonium precipitates. When the ammonium chloride was very dilute, it was necessary to employ as much as 2 litres of solution in order to obtain a quantity of precipitate sufficient for analysis. From the more concentrated solutions of ammonium chloride, the precipitate began to be formed at fairly high temperatures, whereas from dilute solutions it did not separate until the temperature of the laboratory was reached. The precipitate was collected, washed, and analysed by the method described above. The composition of the precipitate varied only slightly with the amount of ammonium chloride in the solution and the temperature at which it was formed.

Gram of NH_4Cl in 100 grams of water.	Temperature of precipitation.	Percentage composition and atomic ratios for solid phase. N.	Hg.	Cl.
1	50—30°	2·83 [1]	75·38 [1·86]	—
1	30—15	2·95 [1]	74·66 [1·79]	—
0·3	30—15	—	75·80	—
0·3	30—15	2·76 [1]	75·60 [1·91]	—
0·3	30—15	2·83 [1]	75·50 [1·87]	—
0·5	30—20	2·78 [1]	75·60 [1·90]	20·63 [2·91]

$HgCl_2,H_2NHgCl$ requires N = 2·675; Hg = 76·61; Cl = 20·32 per cent.

The approximate constancy of the composition of the precipitate obtained under such varying conditions of temperature and concentration of the liquid phase proves that it is a single phase, whilst the fair agreement of the atomic ratios with those of the compound $HgCl_2,H_2NHgCl$ shows that it can be regarded as this compound with small amounts of the constituents of the solution in solid solution.

Conclusion.

(1) A new additive compound of mercuric chloride and ammonia of the formula $3HgCl_2,2NH_3$ has been prepared.

(2) Strömholm's statement that a compound, $Hg_2Cl_3NH_2$, exists has been confirmed.

SIR LEOLINE JENKINS LABORATORY,
JESUS COLLEGE,
OXFORD.

[*Received, November 8th*, 1917.]

XI.—"*Spark-lengths*" *in Hydrocarbon Gases and Vapours.*

By ROBERT WRIGHT.

IN a former paper (T., 1917, **111**, 643), the spark-lengths obtained in various substances were compared with those in air, the temperature, pressure, form of spark-gap, and voltage being the same in each comparison. In the present work, similar measurements have been made for hydrogen, benzene, toluene, and several of the paraffin hydrocarbons, the method employed being identical with that already described.

Each result tabulated is the mean of three or more measurements, which often differed considerably amongst each other, seldom by less than 10 per cent. Still, it is obvious that increase of molecular weight in the series is attended by increase in insulating power, the sole exception noticed being that of *iso*-pentane, which would seem to offer a considerably higher resistance to the passage of the electric discharge than the normal compound, or, indeed, than the following member of the series. The spark-lengths obtained for benzene and toluene are practically identical, and do not differ greatly from that shown by hexane. All measurements were carried out at 138°.

Substance.	Air-gap = 30 mm.	Air-gap = 20 mm.
Hydrogen	80	55
Methane	31	22
Ethane	25	18
Propane	20	15
n-Butane	16	13
n-Pentane	14	11
*iso*Pentane	10	8
Hexane	12	10
Heptane	9	6
Benzene	13	9
Toluene	12	9

The measurements were carried out at the request of Dr. R. V. Wheeler, who supplied all the paraffins employed. The substances used were prepared and purified as follows: *Hydrogen:* prepared from zinc and sulphuric acid, the gas being passed through a series of U-tubes containing glass beads moistened with (*a*) lead nitrate, (*b*) silver sulphate, (*c*) potassium hydroxide. *Methane:* natural marsh gas from a blower in South Wales, purified by liquefaction (CH_4=99·5 per cent.). *Ethane:* from zinc ethyl by the action of water, purified by liquefaction (C_2H_6=99 per cent.). *Propane* and n-*butane:* by the action of nascent hydrogen, from zinc dust and dilute hydrochloric acid, on the corresponding alkyl iodides, purified by liquefaction. The propane contained 98 per cent. of the pure substance and the butane 99·6 per cent. *Pentane* and iso*pentane* were pure liquids obtained from Kahlbaum. *Hexane* and *heptane* were fractionated from petroleum, and each sample consisted of a mixture of isomerides. *Benzene:* this was a pure sample obtained from Kahlbaum. *Toluene:* the sample was fractionated from the commercial product and boiled at 110°.

CHEMICAL LABORATORY,
QUEEN'S UNIVERSITY,
BELFAST.

[*Received, December 10th,* 1917.]

XII.—*Vacuum Balance Cases.*

By Bertram Blount and William H. Woodcock.

In a recent paper (Blount, T., 1917, **111**, 1035), it was shown that whereas it is generally accepted that a balance by a maker of the highest repute should indicate with certainty a difference of 1 part in 2,000,000, say 0·1 milligram with a load of 200 grams in each pan, yet as a fact six balances of the best kind procurable, tested by three skilled observers at two places, under the most careful conditions and with standard weights, showed variations of 0·4 to 1·6 milligrams over four months.

This fact was ascertained in the course of a research begun about three years ago and, unfortunately, interrupted by the War. At the beginning of the research, the accuracy and constancy of the balance were taken for granted, particularly as so moderate a sensitiveness as 0·1 milligram with a load of 200 grams in each pan was sufficient for the purpose in view.

The main object of the research made it necessary to weigh with the degree of accuracy already mentioned in any gas inert towards the materials composing the balance and the matter to be weighed, or in a vacuum, with approximately the same ease as ordinary chemical and physical weighings are performed in balance cases of the usual construction.

Little work of the kind has been done in this matter, although various vacuum balance cases have been made. Before beginning the work, all recorded instances were investigated, and by the kindness of Mr. Wilfred Airy we were allowed to examine the vacuum balance at the Board of Trade.

Of all the published accounts, the only paper which was of use to us was that of Crookes (*Phil. Trans.*, 1873, **163**, 277). Sir William Crookes explained the whole matter to us personally, and we here record our great sense of obligation to him.

We wished, however, to improve on what had been done, and with the aid of Messrs. Casella, the well-known instrument makers, designed a balance case in which the ordinary wooden balance case was reproduced in every essential, but in gun-metal (Figs. 1 and 2). The top is of plate-glass about 1·9 cm. thick, sufficient to withstand atmospheric pressure when the case is exhausted. The door, which is of plate-glass in a gun-metal frame, is carried on a loose hinge and can be brought up square with the case and tightly closed by means of thumb-screws. All surfaces are scraped as for a surface plate. The glass top carries a pressure of 750

kilos. and the front about 1000 kilos. The mode of raising and lowering the beam is precisely that used for the ordinary analytical balance, but as the balance case must be air-tight, the cam shaft passes through a stuffing box. In like manner, the rider-rod passes through a stuffing box, and as it was found impossible to get this tight with the ordinary movements of a rider-rod, an arrangement by which the rider could be moved by a screw motion was adopted.

The first test showed that the case was not tight. It was naturally supposed that this was due to inaccuracy of mechanical fitting, and various methods of making the surfaces come physically together were tried.

The ordinary mechanical mode of making a tight joint between two metal surfaces is to insert a ring or washer of a softer metal. Lead appeared to be unsuitable, as it might be corroded, so gold was tried as a similar plastic metal. It may be remarked that pure gold is extremely difficult to handle, and many hours were spent in fitting the gold washers accurately to the gun-metal case.

This mode of making the case tight was a failure. Re-machining and scraping of the metal surfaces caused little improvement. Ultimately, it was found that the metal was so porous that to maintain a vacuum within it was impracticable. Accordingly, the gun-metal case was tinned by immersion in a bath of molten tin, and was still porous. It was then enamelled both inside and out, and leakage considerably reduced. We were, of course, aware that gases find their way through metal under high pressure, but were surprised at the large leakage which occurs with such an alloy, mechanically sound and with its pores well blocked with tin, at so small a pressure as 1 kilo. per sq. cm.

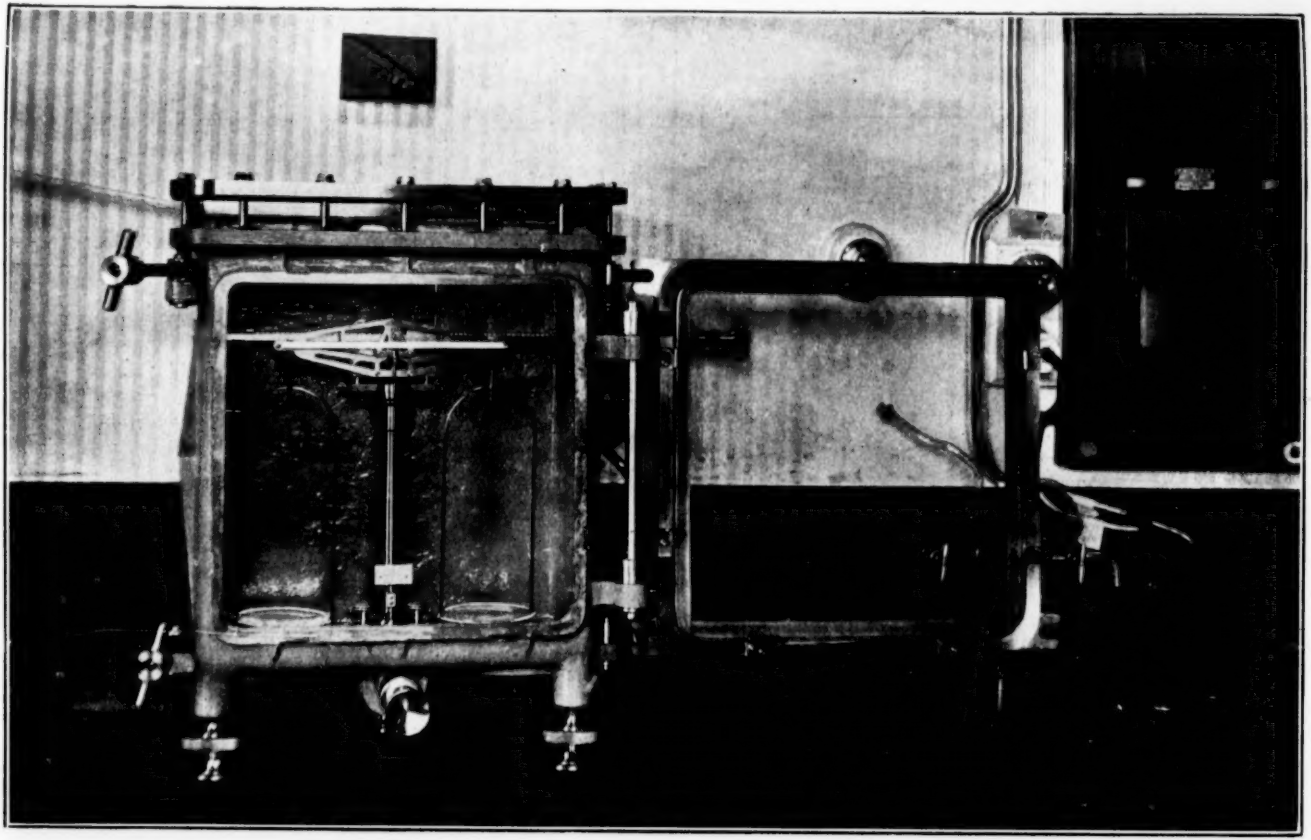
As mentioned above, washers were made of very pure and soft gold, and every effort was tried to construct a case satisfactory from an engineering point of view. These efforts failed, and the methods of the chemist had to be adopted. The plate-glass top and door, instead of being fitted to a scraped gun-metal surface, were made tight with vacuum grease applied to the same surfaces. The gun-metal cocks, two sets of which were tried, were abandoned in favour of glass. With these improvements, the case was fairly satisfactory.

Using a Gaede pump, we were able to obtain a fair vacuum with a leakage of somewhat less than 0·01 mm. per hour. It was necessary, for the object in view, to obtain and keep a vacuum of something like 0·001 mm. for an hour without the continued or renewed use of a pump. In short, it was constancy of condition that was sought.

With all its defects, the metal vacuum case has certain merits.

FIG. 1.

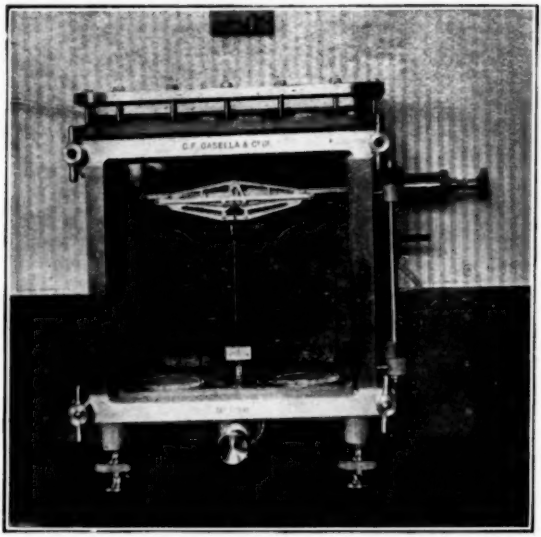
FIG. 1.



GUN-METAL VACUUM BALANCE CASE, WITH DOOR SHOWN OPEN.

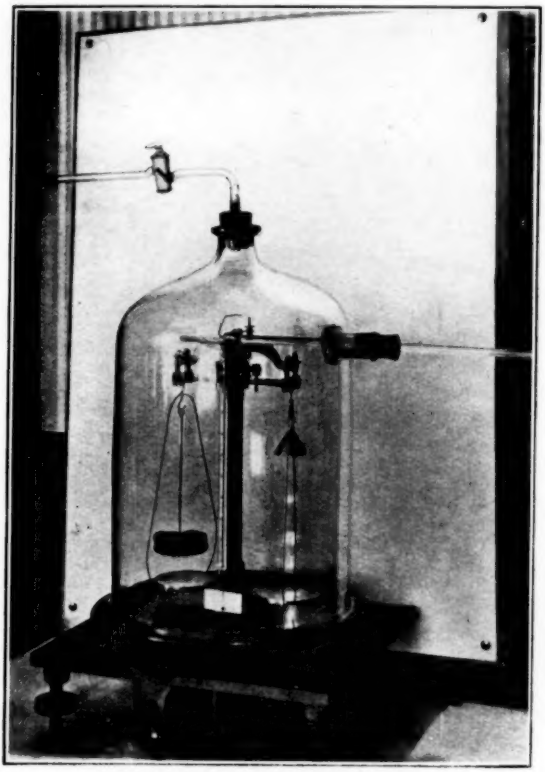
[*To face p.* 82.]

FIG. 2.



GUN-METAL VACUUM BALANCE CASE WITH DOOR CLOSED.
Rider rod on right with screw travel and vertical motion.

FIG. 3.



GLASS VACUUM BALANCE CASE.
Glass rider rod on right ground to fit parallel in glass tube, allowing travel and vertical motion.

It is as near an approach to the ordinary analytical balance, operated in the same way but capable of being used in any given atmosphere (provided it is not corrosive), as has been designed, to the best of our knowledge. It can be used as readily with a moderate plenum as with a vacuum. The shifting of both the main weights and the rider can be easily effected with the single necessity of renewing the atmosphere (or vacuum) when the main weights are moved, in which it is intended to work. With modern methods of producing a vacuum or introducing gases from cylinders containing them under pressure, these operations present no difficulty. It may be noted that all such proceedings take time, and any want of constancy of the balance itself will nullify the results of whatever experiment is in hand.

As it seemed impracticable to make a metal case gas-tight, it was decided to use glass wherever possible. A bell-jar suggested itself as a suitable case for the balance. The size was a difficulty, and the largest procurable had no side tubulus. Accordingly, one was blown on, and we owe thanks to Messrs. Cossor for accomplishing a difficult piece of work (Fig. 3). The bell-jar was ground to fit a thick glass plate carried on a gun-metal plate. Through the middle of the two plates was a tube by which the rising and falling of the beam of the balance could be controlled. A Bunge balance with a 15 cm. beam was used, as we could obtain no bell-jar that would cover a balance with a longer beam. The rider was controlled by a rider-rod capable of the same free movement as that of the ordinary analytical balance; eventually the principle of the ordinary glass hypodermic syringe, used without packing, was adopted, and again we have to thank Messrs. Cossor for accomplishing a difficult piece of work.

The all-glass hypodermic syringe consists of a glass plunger ground to fit the outer tube of the syringe. It is fairly easy to grind conical surfaces to fit, but grinding cylindrical surfaces to a similar accuracy is not so simple and becomes difficult when the material is glass. The difficulty is much enhanced when the length of the cylindrical surfaces is increased. The all-glass hypodermic syringe is a cheap and effective apparatus, but it is only about 5 cm. long and has only a small opening at one end. It was necessary to make a glass rod, ground to fit a glass tube, with such accuracy as to be almost vacuum-tight, having a travel of 25 cm. It would be tedious to record the failures, but at length something which achieved its purpose was prepared.

The outcome of these attempts must be regarded as a success. The balance case can be exhausted to within 0·001 mm., and this vacuum can be kept for more than an hour. The rider can be

moved with the same ease as that of a balance in an ordinary case. The shifting of the larger weights involves breaking the joint between the bell-jar and the plate to which it is ground—a distinct drawback—and a cause of delay. For all that, however, it is an apparatus which may prove useful for the kind of research on which we are intent.

All that is necessary now is a balance which will fit into this case and give constant readings for, say, a year with an accuracy of not less than 1 part in 2,000,000 (0·1 milligram on 200 grams in each pan), and we venture to think that it is not beyond the power of our balance makers to build such an instrument.

76, York Street,
Westminster, S.W. [*Received, November 30th*, 1917.]

XIII.—*The Constitution of Carbamides. Part V. The Mechanism of the Decomposition of Urea when Heated in Solution with Alkalis and with Acids respectively. The Hydrolysis of Metallic Cyanates.*

By Emil Alphonse Werner.

When urea, dissolved in a solution of barium hydroxide, was heated, ammonia was evolved as soon as the boiling point was reached, whilst several minutes elapsed before opalescence, due to separation of barium carbonate, appeared. This observation showed that carbon dioxide and ammonia were not simultaneously evolved at the outset of the decomposition, as indicated by the usual equation, adopted to express the change, namely,

$$CON_2H_4 + Ba(OH)_2 = BaCO_3 + 2NH_3.$$

This fact was much more marked when a quantitative examination was made. Thus, when urea and barium hydroxide, in equal molecular proportions, were heated at 100° for two hours in aqueous solution at concentration $N/7$, the amount of ammonia evolved was equivalent to 20·5 per cent. of "hydrolysis," whilst the proportion of barium carbonate precipitated corresponded with only 12·5 per cent. of change, calculated on the basis of the above equation.

It is obvious that the usual interpretation of this reaction is an erroneous one, and it furnishes but another illustration of the manner by which a decomposition of urea has been accepted almost

a priori on the basis of the carbamide configuration without a proper investigation of the change.

The expression 'hydrolysis of urea,' which is generally used with reference to the above decomposition, has been purposely avoided in giving a title to the present paper, since it has been clearly shown that urea was not directly hydrolysed when decomposed in the presence of acids or alkalis.

The relation which exists between urea and ammonium cyanate is a very simple one, namely, whilst the latter is produced from the union of ammonia with cyanic acid in the 'enol' form (HO·CN), urea is the result of the union of ammonia with cyanic acid in its 'keto' form (HN:CO) (T., 1913, **103**, 1013, 2276).

Herein lies the true difference between the two isomerides. When careful attention is given to the fact that dissociation into ammonia and cyanic acid is the first change which accompanies the action of heat on urea, all phenomena connected with its decomposition in solution, either alone or in the presence of acids or alkalis, are easily explained.

An isomeric transformation of urea, as a preliminary to its decomposition, as suggested by Fawsitt (*Zeitsch. physikal. Chem.*, 1902, **41**, 601) and by Burrows and Fawsitt (T., 1914, **105**, 609), is a quite unnecessary assumption.

Decomposition of Urea in Aqueous Solution in the Presence of Acids.

This change is represented thus:

Phase I. $HN{:}C\langle^{NH_2}_{O} + HCl = NH_4Cl + (HNCO \rightleftharpoons HOCN)$

Phase II. $(HNCO \rightleftharpoons HO{\cdot}CN) + H_2O + HCl = NH_4Cl + CO_2$.

Since cyanic acid is very rapidly hydrolysed, the velocity of the whole reaction will be regulated by the rate of dissociation of urea (at 100°), when both products of dissociation are removed practically as fast as they are generated.

The basic property of urea is much more pronounced than that commonly associated with acid amides, a fact which in itself may be used as an argument against such a structure,* and when hydrochloric acid is added to an aqueous solution of urea, an equilibrium is established between the base and its hydrochloride. Thus, in a normal solution, Walker and Wood (T., 1903, **83**, 484) found that 45 per cent. of urea hydrochloride was undissociated, a condition

* In this respect urea bears a much greater resemblance to the amino-acids, a type of constitution which is implied by the cyclic formula.

which, according to the author's views, is represented by the following equation:

$$HN{:}C\langle \begin{matrix} NH_3 \\ | \\ O \end{matrix} + HCl \quad \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \quad HN{:}C\langle \begin{matrix} NH_2,HCl \\ | \\ OH \end{matrix}$$

55 per cent. 45 per cent.

Now, since it is only 'free' urea which gives rise to the first phase of the decomposition, the velocity of the change might be expected to diminish with an increase in the concentration of hydrochloric acid. This, however, would be only slightly perceptible at all concentrations much below normal, since by far the greater part of the urea would be in the free state at the outset, and hence only a small amount of change in direction (*b*) would be involved throughout the whole progress of the reaction.

If, on the other hand, most of the urea was 'fixed' at the outset as urea hydrochloride, the velocity of the change would be determined by the diminished rate of dissociation of free urea at low concentration, and this would be maintained fairly constant up to a certain point,* since the change in direction (*b*) would only keep pace with the rate of disappearance of free urea.

The following results, which were obtained by heating solutions of urea with hydrochloric acid to the boiling point under reflux, will suffice to illustrate the points just mentioned.

TABLE I.

(I.) Urea, *N*/5; HCl, *N*/2·5. Molecular ratio, 1:2.

Time.		Urea decomposed.	Time.		Urea decomposed.
1 hour	=	21·25 per cent.	5 hours	=	63·75 per cent.
2 hours	=	33·50 ,,	6 ,,	=	68·90 ,,
3 ,,	=	44·50 ,,	7 ,,	=	78·50 ,,
4 ,,	=	59·25 ,,	8 ,,	=	79·25 ,,

(II.) Urea, *N*/5; HCl, *N*/5. (Equal mols.)

Time.		Urea decomposed.
1 hour	=	22·0 per cent.
2 hours	=	34·5 ,,
3 ,,	=	47·00 ,,
222 minutes	=	50·0 ,,

(III.) Urea, N/2·5; HCl, N/2·5.

Time.		Urea decomposed.
1 hour	=	25·0 per cent.
2 hours	=	44·75 ,,
145 minutes	=	50·0 ,,

A comparison of the results under (I) and (II) (urea = *N*/5) shows the effect of an increase in the concentration of hydrochloric

* The neutralisation of free acid by ammonia would naturally exert a disturbing effect on the above equilibrium, which would be more marked at the higher concentration.

acid in lowering the velocity of the change; the difference was most marked during the third hour, that is, when the concentration of hydrochloric acid, in the case of (II), was very low as neutralisation was approached, since the maximum amount of urea that could be decomposed* in the presence of one molecular proportion of hydrochloric acid is only half of the total present, on account of the simultaneous progress of the two phases of the reaction. The long period required to decompose urea when two molecular proportions of hydrochloric acid were present was due to the slow dissociation of urea as its concentration diminished, and the results show that the velocity of the change was determined solely by the concentration of 'free' urea. The results under (III) furnish additional proof of this; thus it will be noticed that the maximum amount of urea ($N/2{\cdot}5$) was decomposed in 145 minutes, as compared with 222 minutes, which were required to effect the same amount of change when the concentration of urea at the outset was at $N/5$ (II).

Fawsitt found that it required 2600 minutes to decompose all urea in a solution which contained at the outset urea ($N/8$) and hydrochloric acid ($N/2$), that is, four molecules of acid to one of urea.

Decomposition of Urea in Aqueous Solution in the Presence of Sodium Hydroxide.

Since the acidic property of urea is very feeble, when sodium hydroxide is added to its aqueous solution, an equilibrium represented as follows:

$$HN{:}C\begin{cases}NH_2\\O\end{cases} + NaOH \rightleftharpoons HN{:}C\begin{cases}NH_2\\ONa\end{cases} + H_2O,$$

would only obtain to a small extent when the concentration of both was very high. In solutions below normal, for example, it is certain that nearly if not all the urea would be in the free state. Therefore, according to the dissociation theory, the velocity of decomposition of urea in the presence of sodium hydroxide should be greater than in the presence of hydrochloric acid at all concentrations.

This has been found to be the case, which is contrary to the general result arrived at by Fawsitt (*loc. cit.*). The two phases

* That is, within a comparatively short time, up to the point of neutralisation of the acid. Fawsitt found that in a solution of urea alone ($N/2$), decomposition to the extent of 98·9 per cent. required 450 hours at 99–100°.

of this reaction, which were easily distinguished experimentally, may be represented as follows:

Phase I. $HN{:}C\!<\!\begin{matrix}NH_2\\ |\\ O\end{matrix} + NaOH = NH_3 + NaOCN + H_2O.$

Phase II. (*a*) $NaOCN + 2H_2O = NH_3 + NaHCO_3.$

In the first phase, cyanic acid is temporarily fixed as alkali cyanate; hydrolysis of the latter quickly follows, and the two phases continue to proceed simultaneously with velocities which vary as the conditions change during the progress of the reaction.

During the earlier stages, sodium cyanate accumulates in considerable quantity in solution, since the velocity of its formation in the first phase is much greater than the speed of its disappearance (by hydrolysis) in the second phase. As the concentration of urea diminishes, the velocity of its dissociation is exceeded by that of the hydrolysis of the alkali cyanate, and hence in the later stages the second phase becomes the predominant change.

The different results obtained after heating urea in solution with sodium hydroxide, under such conditions that ammonia was removed as it was evolved, whilst the concentration was maintained as nearly constant as was possible, are given in the following tables.

The proportion of change under phase I corresponds with the amount of alkali cyanate found in the cold solution at the end of an experiment, whilst phase II represents the amount of alkali cyanate which had been hydrolysed during the progress of the reaction, calculated from the amount of ammonia evolved, after the necessary correction, on the basis of equation (*a*), phase II.

TABLE II.

Urea, $N/5$; sodium hydroxide, $N/5$. Molecular ratio, 1:1.

Time.	Phase I.	Phase II.	Urea decomposed.
1 hour	17·7 per cent.	4·40 per cent.	22·10 per cent.
2 hours	30·8 „	9·0 „	39·80 „
3 „	36·0 „	18·25 „	54·25 „

TABLE III.

Urea, $N/2{\cdot}5$; sodium hydroxide, $N/2{\cdot}5$. Molecular ratio, 1:1.

Time.	Phase I.	Phase II.	Urea decomposed.
1 hour	21·25 per cent.	4·15 per cent.	25·40 per cent.
2 hours	32·00 „	10·00 „	42·00 „
3 „	38·90 „	18·80 „	57·70 „
4·5 „	36·05 „	48·72 „	84·77 „

TABLE IV.

Urea, $N/5$; sodium hydroxide, $N/2{\cdot}5$. Molecular ratio, 1:2.

Time.	Phase I.	Phase II.	Urea decomposed.
1 hour	19·05 per cent.	4·52 per cent.	23·57 per cent.
2 hours	27·50 „	13·12 „	40·62 „
3 „	35·35 „	19·82 „	55·17 „
4 „	36·10 „	28·95 „	65·05 „

TABLE V.

Urea, $N/5$; sodium hydroxide, N. Molecular ratio, 1:5.

Time.	Phase I.	Phase II.	Urea decomposed.
1 hour	20·0 per cent.	6·75 per cent.	26·75 per cent.
2 hours	28·9 „	16·55 „	45·45 „
3 „	34·2 „	27·65 „	61·85 „

When the above results are compared with those recorded under table I, it will be seen that the proportion of urea decomposed was greater in the presence of sodium hydroxide than in the presence of hydrochloric acid at similar concentrations.

Whilst the foregoing results are in perfect agreement with the dissociation theory of the mechanism of the change, they appear as a contraversion of the conclusions arrived at by Fawsitt (*loc. cit.*), who found that unless the concentrations of alkali was very high (and that of urea relatively so), the velocity of the change was greater in the presence of hydrochloric acid than in the presence of sodium hydroxide.

All Fawsitt's experiments were made in sealed tubes, and herein lies the cause of the discrepancy, which supplies further evidence in support of the present theory. It is obvious that accumulation of ammonia in solution under pressure would seriously check the dissociation of urea, and so retard the change to an extent which would have no parallel in the case of the decomposition in the presence of an acid, where both dissociation products were removed as fast as they were generated. Thus, when urea and sodium hydroxide, in equal molecular proportions and at concentration $N/5$, were heated for three hours at 100° in a sealed tube, only 33 per cent. of urea was decomposed, as against 54·25 per cent. (exp. 3, table II) when the experiment was performed in an open vessel, all other conditions being equal. It should be noticed that the amount of urea decomposed in the former case is also considerably less than that decomposed in the presence of hydrochloric acid ($N/5$) in an open vessel [table I, (II)].

When the relative effects of acids and alkalis on the velocity of the decomposition of urea are considered, there can be no doubt that in Fawsitt's experiments, on account of the use of sealed tubes, a departure from comparable conditions was quickly brought about.

As a matter of fact, Fawsitt showed that the decomposition of urea was retarded by the presence of ammonium hydroxide or ammonium chloride, whilst such salts as sodium chloride and potassium chloride, although they had but little effect in very dilute solutions, produced a marked increase in the speed of decomposition at normal concentration. Other 'catalysts,' including platinum-black, were found to be without effect, and in the obscure light of the isomeric transformation theory, no explanation could be offered.

The effects in question are obviously in complete agreement with the dissociation theory, which they help to confirm.

Decomposition of Urea in Aqueous Solution in the Presence of Barium Hydroxide.

This reaction was originally proposed by Bunsen as a method for the estimation of urea, based on the amount of barium carbonate formed. As is well known, severe conditions are required to complete the change, namely, very prolonged heating, a high temperature (180—200°), and an excess of barium hydroxide.

It is curious, in view of the above, that the progress of this decomposition has apparently not been investigated.

The two phases of the reaction are represented thus:

Phase I. $2HN{:}C\!<\!\begin{matrix}NH_2\\ |\\ O\end{matrix} + Ba(OH)_2 = Ba(OCN)_2 + 2NH_3 + 2H_2O.$

Phase II. { (*b*) $Ba(OCN)_2 + 3H_2O = BaCO_3 + 2NH_3 + CO_2$, and
(*c*) $Ba(OCN)_2 + 2H_2O = BaCO_3 + CON_2H_4$.*

The following results were obtained when urea and barium hydroxide in equal molecular proportions were heated at 100° in aqueous solution, and whilst ammonia was removed as it was evolved.

* See page 94

TABLE VI.

Urea, $N/8$; barium hydroxide, $N/8$.

Time.	Phase I. Per cent.	Phase II. Per cent.	Urea decomposed. Per cent.	Calculated on the usual equation. $BaCO_3$ precipitated. Per cent.	Calculated on the usual equation. NH_3 evolved. Per cent.
1 hour ...	16·0	3·0	19·0	6·0	11·0
2 hours ...	23·9	8·55	32·45	12·5	20·5
3	28·7	15·15	43·85	18·5	29·5
4 „	29·9	17·55	47·45	22·5	32·5

The numbers in the two last columns are given to prove the fallacy underlying the usual interpretation of the change. Thus, after one hour, whilst the amount of barium carbonate formed indicated the decomposition of only 6 per cent. of the urea originally present, the ammonia evolved was equal to the decomposition of 11 per cent.; in reality, the amount of urea which had been decomposed was equal to 19 per cent., that is, 8 per cent. of the nitrogen of urea was present in solution as barium cyanate.

In these experiments, phase II commenced (judged from the sudden appearance of opalescence) about seven minutes after phase I had been in progress. Since one molecular proportion of barium hydroxide can theoretically complete the decomposition of two molecular proportions of urea, the results of the two phases should be compared with those under table IV. When the true mechanism of the change is brought to light, it can be readily understood why such severe conditions have been found necessary in order to estimate urea by means of this reaction.

The Stability of Urea in Aqueous Solution and in the Presence of Acid, and of Alkali in the Cold.

After a solution of urea has been heated for a few minutes at 90—100° and subsequently cooled, the presence of the cyanate radicle can be readily proved on addition of silver nitrate. This well-known fact is not explained by the usual ionic theory. Fawsitt found that 450 hours were required to decompose and hydrolyse 98·9 per cent. of the urea originally present in a semi-normal solution at 99°.

If the dissociation products could persist at a constant temperature an equilibrium, represented thus,

$$HN{:}C\begin{cases}NH_2\\O\end{cases} \rightleftharpoons HN{:}CO + NH_3 \rightleftharpoons HO{\cdot}CN \rightleftharpoons NH_4{\cdot}OCN,$$

would obtain, and the decomposition of urea and of ammonium cyanate would be completely arrested. The velocity of the change is determined by the very slow hydrolysis of cyanic acid under highly unfavourable conditions, whilst dissociation of urea is checked in consequence.

The progress of the change may be mentally compared to the working of a syphon in which the flow of liquid through the downward tube is seriously checked by a very narrow outlet.

Since urea is not dissociated in solution at the ordinary temperature, an equilibrium between it and ammonium cyanate can only arise on the application of heat. Judging from certain statements in the literature of the subject, the views on this point do not appear quite clear, since it is sometimes stated that the equilibrium is independent of the temperature.

In order to settle the question, a solution of pure urea ($N/2$) in distilled water sterilised by saturation with toluene was tested from time to time with silver nitrate and with barium hydroxide respectively. After nine months, the solution was still neutral, and a negative result was obtained with each reagent.

A similar solution of urea in non-sterilised water gave a marked opalescence with the respective reagents after fourteen days. At the end of six months, the solution contained ammonium carbonate, but no ammonium cyanate, since, after precipitation with barium hydroxide, the carefully neutralised filtrate gave no precipitate on the addition of silver nitrate. This latter result is of interest, since the decomposition of urea in this case was unquestionably brought about, through the agency of urease, by micro-organisms* which had developed in the solution.

A solution of urea ($N/2$) in pure sodium hydroxide ($N/2$) solution, after remaining at the laboratory temperature for five months, showed no change; at the end of twelve months a trace of the cyanate radicle was detected.

A solution of urea in the presence of hydrochloric acid under similar conditions remained unchanged.

Urea therefore does not undergo an isomeric change until the temperature of its dissociation is reached.

Note on the Decomposition of Urea by Urease.

The ease with which urea is decomposed by urease, even at 15—20°, is in striking contrast to its stability in the presence of acids or of alkalis at the same temperature, or when heated alone

* The mycelium of a specific mould was observable in the solution.

in solution. When the remarkable* 'selective' action of the enzyme is remembered (Armstrong and Horton, *Proc. Roy. Soc.*, 1912, **85**, 109), this fact must be considered as additional evidence in favour of a molecular structure of urea peculiar to itself, as shown by the cyclic formula.

It seems probable that the zymolysis of urea is a true case of direct hydrolysis, independent of dissociation as a preliminary to the change. Urease was not found to have an accelerating effect on the hydrolysis of potassium cyanate, nor has it been found possible, so far, to detect the cyanate radicle during the decomposition of urea by the enzyme. The suggestion put forward by Armstrong and Horton (*loc. cit.*) that urease, the solution of which they noted was acid to phenolphthalein, probably acts by combining with urea in virtue of the basic character of the latter, is open to doubt. Urease is markedly amphoteric, a fact which, so far as the author is aware, has not been generally recognised. The alkalinity of a solution of the enzyme towards methyl-orange was found to be greater than its acidity towards phenolphthalein.

The Decomposition of Urea in the Presence of Alcohol.

Burrows and Fawsitt (*loc. cit.*) found that the addition of alcohol to a solution of urea ($N/10$) + hydrochloric acid ($N/10$) produced a marked decrease in the velocity of decomposition. This result, they state, "was not exactly what we anticipated," since "alcohol increases the velocity of transformation of ammonium cyanate into urea, and the decomposition of urea is closely related to its formation." The latter remark, of course, is only true so far as the change (dissociation) which gives rise to the first phase of its decomposition is concerned.

The addition of alcohol should undoubtedly produce an increase in the velocity of the decomposition of urea if this is solely dependent on its dissociation and all other conditions are the same. A consideration of the conditions implied by the equilibrium scheme just given will show why this result is not effected. Since alcohol promotes the dissociation of ammonium cyanate, it must also inhibit to a corresponding degree any tendency to its formation at all temperatures above its dissociation point, and hence its presence brings about a limitation on one side which counterbalances its promotive effect on the other. The ulterior effect of

* The behaviour of urease towards seventeen different amino- and imino-compounds, presumably more or less related to urea in constitution, has been examined. In no case was there evidence of decomposition.

alcohol will therefore depend on its power of facilitating or retarding the removal of one or other of the dissociation products, and since a check on the rate of hydrolysis of cyanic acid will be the effect, as suggested by Burrows and Fawsitt from a somewhat different point of view, the velocity of the decomposition of urea will be retarded in consequence. The increased pressure produced by alcohol, particularly at high concentration, and at the higher temperature (98·2°), would also check dissociation of urea.

In the conversion of ammonium cyanate into urea, the promotive effect of alcohol is in no way interfered with, since both dissociation products are removed with great rapidity by the formation of urea at a temperature much below its dissociation point, and hence there is little or no opportunity for hydrolysis of cyanic acid.

It is interesting to note the very much greater velocity of decomposition of urea at 98·2° as compared with that at 71·25° and at 61·05° found by Burrows and Fawsitt. The respective values are represented by the ratios 83·6, 2·77, and 0·715. The fact that urea only commences to dissociate in solution at a fair degree of rapidity above 90° explains the cause of this wide difference.

Mechanism of the Formation of Urea during the Hydrolysis of Metallic Cyanates.

O. and J. Masson (*Zeitsch. physikal. Chem.*, 1910, **70**, 290) have shown that the hydrolysis of potassium cyanate at 80° was completed, in accordance with the equation:

$$(d)\quad 4KOCN + 6H_2O = 2K_2CO_3 + (NH_4)_2CO_3 + CON_2H_4,$$

whilst in the case of barium cyanate the whole of the nitrogen appeared in the form of urea, as represented by equation (*c*) (p. 90).

Ionisation of the cyanate being assumed as the first step, O. and J. Masson have accounted for the formation of urea thus:

$$(A)\quad CNO' + 2H_2O \longrightarrow NH_4^{\cdot} + CO_3''.$$
$$(B)\quad CNO' + NH_4^{\cdot} = CON_2H_4.$$

A somewhat similar suggestion has been offered by Normand and Cumming (T., 1912, **101**, 1859) to explain the formation of urea when pure cyanic acid was hydrolysed in dilute solution, thus:

$$(C)\quad 2H^{\cdot} + 2CNO' + 2H_2O = CON_2H_4 + CO_2.$$

It was suggested, because the alkali cyanates show a neutral reaction, that cyanic acid must be a strong acid, and would, there-

fore, be highly ionised in dilute solution. From this suggestion the author ventures to differ. Alkali nitrites, for example, have a neutral reaction, yet nitrous acid is an extremely weak acid, $K = 6 \times 10^{-4}$, according to Rây and his co-workers (T., 1917, **111**, 414). The properties of cyanic acid are distinctly those of a feeble acid, and the ease with which its ammonium salt is dissociated, whereby urea is formed, is a fact which bears directly on the immediate question.

It must be admitted that an ionic theory, such as is represented by equation (*B*), originally proposed by Walker, or by (*C*), fails to throw any light on the mechanism of the change, since no attempt has been made to show in what way urea is formed from the interaction of the respective ions $NH_4^{\cdot}$ and CNO'. With the deceptive 'carbamide' structure in view, it has evidently been considered useless to attempt to pursue the mysterious changes by which the ions effect such a result. Now an ionic theory is not in agreement with the facts; Walker found, contrary to expectation, that the velocity of the transformation of ammonium cyanate into urea was greater in the presence of alcohol than in the presence of water, and since there must be fewer ions present in the former condition, it has been assumed that the velocity of the interaction (*B*) must be greater in the presence of alcohol. It must be conceded that this is but a speculation, to meet a fact, rather than an explanation. Since alcohol will promote dissociation of ammonium cyanate, whilst diminishing ionisation, the increased velocity of the transformation under such conditions appears as a normal phenomenon in perfect agreement with the author's theory of the change (*loc. cit.*).

The formation of urea from metallic cyanates is explained in a simple manner, on the basis of hydrolytic dissociation * as the first step in the change, thus:

$$KOCN + H_2O \rightleftharpoons KOH + (HOCN \rightleftharpoons HN{:}CO)$$

$$\searrow$$

$$HOCN + H_2O = NH_3 + CO_2 = KHCO_3$$

$$HN{:}CO + NH_3 = HN{:}C\begin{matrix}NH_2\\ |\\ O\end{matrix}, \text{ and } HOCN + NH_3 = NH_4{\cdot}OCN.$$

The following results illustrate how slowly potassium cyanate was hydrolysed in solution at the ordinary temperature.

* Pure potassium cyanate shows a slight alkalinity towards phenolphthalein after immediate dissolution in water.

TABLE VII.

Potassium Cyanate, N/2. Mean $t° = 16°$.

Time.	KOCN hydrolysed.	Time.	KOCN hydrolysed.
7 days	11·4 per cent.	42 days	81·8 per cent.
13 „	22·4 „	49 „	87·8 „
21 „	43·2 „	56 „	91·6 „
28 „	56·8 „	63 „	94·5 „
35 „	69·7 „	70 „	98·7 „

The amount of urea found in solution at the end of ten weeks was 0·94 gram; from 8·1 grams of potassium cyanate, equation (*d*) would require 1·5 grams of urea. The conditions were less favourable for the formation of urea than when hydrolysis was effected at 80°, at which temperature ammonium cyanate would not be formed.

When potassium cyanate was hydrolysed at 100° under reflux, urea was formed to the extent of 18·44 per cent. of the theoretical, equation (*d*). No urea was found when potassium cyanate (*N*/5) was hydrolysed at 100° in presence of sodium hydroxide (*N*/2·5) (Expts. I, II, and III). It may therefore be safely concluded that no urea would be regenerated during the progress of its decomposition in the presence of sodium hydroxide in an open vessel; on the other hand, a condition favourable to its regeneration, to some extent, would be brought about in a sealed tube, more particularly in the later stages of the reaction. This fact must also be taken into account in considering the results obtained by Fawsitt (*loc. cit.*) for the velocity of the decomposition of urea in the presence of alkalis.

EXPERIMENTAL.

As regards the results given under table I, it is only necessary to point out that the titrations of residual acidity after each experiment were made with methyl-orange as indicator. The urea used (0·6 gram in each case) was twice recrystallised from alcohol. All the experiments were made with the same flask and reflux condenser, and a quiet, continuous ebullition was maintained throughout. Each experiment was duplicated.

The following method was adopted in obtaining the results of the decomposition of urea in the presence of sodium hydroxide.

Expts. tables II–V.—0·6 Gram of urea, 10 c.c. of *N*-sodium hydroxide, and 40 c.c. of water (concentration *N*/5) were heated to the boiling point in a distillation flask (150 c.c.) of resistance glass, carrying a stoppered delivery tube, through which a continuous supply of recently boiled distilled water was maintained, so that the volume of liquid was kept, as nearly as possible, constant

throughout the process of distillation. The ammonia evolved was absorbed in an excess of normal acid contained in a suitable receiver attached to a vertical condenser connected with the distillation flask. At the end of an experiment the residual solution was rapidly cooled under the tap; the cyanate radicle was estimated (1) by precipitation with silver nitrate in the neutral solution, after the 'carbonate' had been removed by barium nitrate and barium hydroxide; the excess of silver nitrate was titrated by Volhard's method; (2) by addition of the solution to an excess of hydrochloric acid, which was afterwards titrated, using methyl-orange as indicator. A lower result was almost invariably obtained by this method; this was due to slight loss of cyanic acid, the odour of which was very noticeable when the liquid was added to excess of normal acid; the solution was allowed to remain, until the odour had disappeared, to ensure complete hydrolysis of cyanic acid before titration. The following examples will suffice to show how the values for the two phases were calculated:

$$0{\cdot}6 \text{ gram } CON_2H_4 \longrightarrow 2NH_3 = 20 \text{ c.c. } N\text{-HCl},$$
$$NaOCN = 100 \text{ c.c. } N/10\text{-}AgNO_3.$$

Table III. One Hour.—Ammonia evolved = 2·95 c.c. *N*-HCl. Sodium cyanate present in residual solution = 21·25 c.c. $N/10$-$AgNO_3$. Hence, phase I = 21·25 per cent.; if hydrolysed, this would be obviously equivalent to ammonia = 2·125 c.c. *N*-HCl. Hence, omitting the third decimal number, $(2{\cdot}95 + 2{\cdot}12) \times 5 = 25{\cdot}35$ per cent. of urea decomposed, and $25{\cdot}35 - 21{\cdot}25 = 4{\cdot}10$ per cent. phase II.

Table IV. *Four Hours.*—Ammonia evolved = 9·4 c.c. *N*-HCl. Sodium cyanate present = 36·1 c.c. $N/10$-$AgNO_3$ = 36·1 per cent. phase I; hence, $(9{\cdot}4 + 3{\cdot}61) \times 5 = 65{\cdot}05$ per cent. of urea decomposed; therefore, phase II, $65{\cdot}05 - 36{\cdot}1 = 28{\cdot}95$ per cent.

A second experiment, in which the residual sodium cyanate was hydrolysed [method (2)], gave ammonia = 3·55 c.c. *N*-HCl = 35·5 per cent. phase I; ammonia evolved = 9·45 c.c. *N*-HCl. Hence, 65·0 per cent. of urea decomposed, and phase II = 29·5 per cent.

Whilst no great accuracy is claimed for the values representing each phase, on account of the difficulty experienced in maintaining the volume of solution constant, the order of the results, so far as the amount of urea decomposed was concerned, can be certainly trusted within 2 or 3 per cent., and since this was one of the chief facts which it was sought to prove, no further useful information was likely to be obtained by extending the time of heating beyond three or four hours.

The following is an example of an experiment with barium hydroxide.

Table VI. Four Hours.—Ammonia evolved = 6·5 c.c. *N*-HCl. Barium carbonate precipitated, neutralised 4·5 c.c. *N*-HCl. Hence (from 0·6 gram of urea) amount of urea decomposed = 32·5 per cent. from ammonia estimation and = 22·5 per cent. from amount of barium carbonate precipitated, calculated on basis of usual equation.

Barium cyanate in residual solution = 29·9 c.c. $N/10$-$AgNO_3$. Hence phase I = 29·9 per cent., and $(6{\cdot}5 + 2{\cdot}99) \times 5 = 47{\cdot}45$ per cent. of urea decomposed, therefore phase II = 17·55 per cent.

Estimation of Urea Formed During Hydrolysis of Potassium Cyanate.

Expt. I.—2·025 Grams of potassium cyanate dissolved in 50 c.c. of water ($N/2$) were boiled under reflux for three hours (crystals of ammonium carbonate gradually formed on the sides of the reflux tube), at the end of which time only 1·3 per cent. of the salt remained unchanged. The residue, after the solution was evaporated to dryness at 100°, was extracted with hot alcohol, and the residue from the latter solution, after removal of all ammonium salt, gave, when decomposed with an excess of alkaline solution of sodium hypobromite in the nitrometer, 28·45 c.c. N_2 at 24° and 764 mm. = 25·5 c.c. N_2 at N.T.P., equal to 0·06825 gram of urea = 18·44 per cent., calculated on equation (*b*). The presence of urea was qualitatively proved by its behaviour towards urease, and precipitation as urea nitrate.

Expt. II.—8·1 Grams of potassium cyanate dissolved in 200 c.c. of water ($N/2$) were allowed to remain for ten weeks at the laboratory temperature; 25 c.c. of the solution, after removal of ammonium carbonate, gave 44·09 c.c. N_2 at N.T.P., equal to 62·99 per cent. of urea formed, on basis of equation (*b*).

Expt. III.—0·81 Gram of potassium, 20 c.c. of *N*-sodium hydroxide, and 30 c.c. of water were boiled for three hours in a distillation flask, whilst the concentration was maintained nearly constant. The residual solution gave no nitrogen when tested as above with alkaline sodium hypobromite.

Summary.

(1) The decomposition of urea when heated in aqueous solution in the presence of acids or of alkalis is primarily dependent on its dissociation into ammonia and cyanic acid.

(2) The so-called 'hydrolysis of urea' under such conditions is no more than the hydrolysis of cyanic acid or of an alkali cyanate,

as the case may be, and hence is not a change which gives any support to a 'carbamide' structure, as so commonly suggested.

(3) Under comparable conditions, the velocity of the decomposition of urea is greater in the presence of sodium hydroxide than in the presence of hydrochloric acid, because the proportion of free urea in solution is greater in the former case.

(4) Whilst an ionic theory fails to throw any light either on the conversion of ammonium cyanate into urea or on the formation of urea during the hydrolysis of cyanic acid or of metallic cyanates, it is not in agreement with the facts.

(5) The effect of alcohol in accelerating the transformation of ammonium cyanate into urea and in retarding the decomposition of urea in solution is easily explained by the dissociation theory, with which it is in perfect agreement.

(6) A sterilised solution of urea does not suffer any 'hydrolysis' or reversion to ammonium cyanate at the ordinary temperature. The latter phenomenon can only arise from the dissociation of urea as a preliminary to the change.

UNIVERSITY CHEMICAL LABORATORY,
TRINITY COLLEGE, DUBLIN. [*Received, October 2nd*, 1917.]

XIV.—*Di*-n-*butylaniline.*

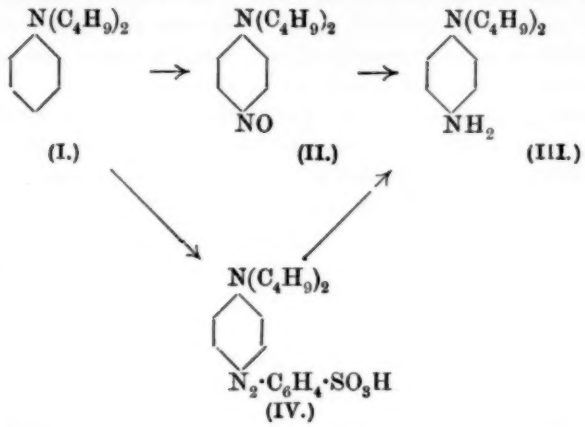
By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

IT has been shown (T., 1917, **111**, 1016) that by heating *n*-butyl chloride and aniline under reflux, *n*-butylaniline is the chief product. This reaction has been further studied, and it has been found that prolonged heating under reflux or the addition of a catalyst such as iodine, favours the production of di-*n*-butylaniline. Its formation was, however, more readily brought about by heating *n*-butyl chloride and aniline under pressure. By heating aniline hydrochloride and *n*-butyl alcohol under pressure, *n*-butylaniline was produced, but this reaction requires a higher temperature and pressure than in the case of *n*-butyl chloride and aniline in order to obtain the same yield.

By repeated fractionation, di-*n*-butylaniline (I) was obtained pure. It was converted into p-*nitrosodi*-n-*butylaniline* (II), which gave additive compounds with certain metallic chlorides.

The nitroso-compound was reduced to p-*phenylenedi*-n-*butyl*-

diamine (III), which, on diazotisation and combination with β-naphthol, furnished *4-di*-n-*butylaminobenzeneazo-β-naphthol*.



Karrer (*Ber.*, 1915, **48**, 1398), in an attempt to prepare *p*-phenylenedi-*n*-butyldiamine from di-*n*-butylaniline, endeavoured to introduce a *p*-nitroso-group into the dialkylaniline, but was not successful; he states that a nitroso-group cannot be introduced into this compound, and that in this respect it differs from the dipropyl- and lower dialkyl-anilines. We have found, however, that Karrer's statement is incorrect. A nitroso-group can be readily introduced into di-*n*-butylaniline, and this *p*-nitroso-derivative has properties somewhat similar to the lower members of the series, but whilst the latter are solid at the ordinary temperature, *p*-nitrosodi-*n*-butylaniline is an oil. Its constitution was proved by its decomposition into di-*n*-butylamine and *p*-nitrosophenol, almost quantitative yields of which being obtained under certain conditions. It was observed that although *p*-nitroso-*n*-butylaniline was very quickly decomposed by alkali, *p*-nitrosodi-*n*-butylaniline was converted more slowly into the amine and nitroso-compound under similar conditions. Karrer next attempted to prepare *p*-phenylenedi-*n*-butyldiamine by another method, namely, to combine diazotised sulphanilic acid with di-*n*-butylaniline, and to reduce the product. He obtained, however, monobutylaminoazobenzenesulphonic acid, which, on reduction, gave *p*-phenylenemonobutyldiamine, and experiments with di*iso*amylaniline gave similar results. Again we obtained different results from those of Karrer. We found that di-*n*-butylaniline combines in quite a normal manner with diazotised sulphanilic acid, yielding *4-di*-n-*butylaminoazobenzene-4′-sulphonic acid* (IV), which, on reduction, gives p-*phenylenedi*-n-*butylaniline*. Diazotised sulphanilic acid reacts

also with mono-*n*-butylaniline, yielding 4-n-*butylaminoazobenzene-4′-sulphonic acid*, and this compound, on reduction, gave *p*-phenylene-*n*-butyldiamine. The two azo-derivatives and the corresponding products of reduction have been compared. The sodium salts of the azo-sulphonic acids differ in the ease with which they crystallise, the di-*n*-butylaminoazobenzenesulphonate being more difficult to obtain in the crystalline condition. The amine dihydrochlorides also differ in their solubilities in alcohol. The amines obtained by reducing the azo-compounds were proved to be identical respectively with the products of reduction of *p*-nitrosodi-*n*-butylaniline and of *p*-nitrosomono-*n*-butylaniline. The two amines are also distinguished by means of their colour reactions with nitrous acid and with ferric chloride. There is the possibility that Karrer was working with di*iso*butylaniline, but from a few experiments carried out, indications were obtained that this compound yields a nitroso-derivative and also couples normally with diazotised sulphanilic acid. Another suggestion is that he was working with a mixture of mono- and di-alkylaniline. A mixture of azo-derivatives would thus be produced on treatment with diazotised sulphanilic acid, and on crystallisation of the sodium salts the mono-*n*-butyl derivative would be obtained, which, on reduction, would give *p*-phenylenemono-*n*-butyldiamine.

Experimental.

By heating aniline and *n*-butyl chloride in molecular proportions for thirty-six hours on the water-bath under reflux, the main product of the reaction has been shown to be mono-*n*-butylaniline. There was also a fraction boiling at 250—270°, which has now been examined. For further investigation, more of this fraction was prepared by heating mono-*n*-butylaniline with one molecular proportion of *n*-butyl chloride under reflux for forty-eight hours. The excess of *n*-butyl chloride was distilled off and the residue rendered alkaline with sodium hydroxide solution. The oil which separated and the ethereal extract of the whole solution were mixed, the resulting ethereal solution was dried, evaporated, and the residue fractionated. Only a small quantity of distillate was obtained boiling below 255°; the fraction boiling between 255° and 265° was collected and further fractionated, when at 260—263°/767 mm., di-*n*-butylaniline distilled as an almost colourless, refractive liquid, which in bulk had a pale yellow tint.

It was found, by heating aniline and *n*-butyl chloride in an autoclave under a pressure of 5—7 atmospheres, that interaction takes place very rapidly; in an hour a 90—95 per cent. yield of

mono-*n*-butylaniline can be obtained. In one experiment, aniline (40 grams) was heated with *n*-butyl chloride (50 grams) at 130—140° in an autoclave for forty-five minutes. The oil which was obtained after the action of sodium hydroxide and treatment in the usual way had the following percentage composition: aniline (estimated as zinc salt), 5·5; mono-*n*-butylaniline (b. p. 232—250°), 90; di-*n*-butylaniline (b. p. 250—260°), 3·5, with a small residue of higher boiling point. By the action of *n*-butyl chloride on mono-*n*-butylaniline under pressure at 180°, a good yield of di-*n*-butylaniline was obtained. When *n*-butyl alcohol and aniline hydrochloride were heated together under pressure, the temperature rising to 200°, mono- and di-*n*-butylaniline were produced. The longer the period of heating, the greater was the quantity of the di-*n*-butyl derivative obtained. The product contained aniline as well as its mono- and di-substituted derivatives. The aniline was removed by heating the mixture with a slight excess of 20 per cent. zinc chloride solution. After well mixing the paste, the insoluble aniline zincichloride was collected, well pressed, and then washed several times with dry ether. The ethereal washings and filtrate were combined, separated from the aqueous layer, and dried, the ether being removed by distillation and the residual oil fractionated. An analysis was made of the fraction referred to above (b. p. 260—263°/767 mm.):

0·1121 gave 0·3380 CO_2 and 0·1134 H_2O. C = 82·23; H = 11·24.
0·1560 ,, 9·4 c.c. N_2 at 19·5° and 751·1 mm. N = 6·95.*
$C_{14}H_{23}N$ requires C = 81·89; H = 11·29; N = 6·82 per cent.

Di-*n*-butylaniline is an almost colourless liquid, lighter than water, which darkens very slowly on keeping; it has a very faint but not unpleasant odour, is miscible in all proportions with alcohol or ether, and is soluble in acids, but practically insoluble in water. When potassium ferrocyanide solution is added to a solution of di-*n*-butylaniline in dilute hydrochloric acid, a white precipitate is obtained which is insoluble in water or ether, and only very sparingly soluble in alcohol. On treatment with fuming sulphuric acid, di-*n*-butylaniline gives a *sulphonic acid*, the *barium* salt of which is readily soluble in water, but practically insoluble in absolute alcohol.

* Using copper oxide in the combustion tube, it was difficult to decompose this compound completely, the nitrogen content appeared to be high and repeated estimations gave varying results. An analysis of the gas collected in the nitrometer in one estimation, after drying showed the presence of 18 per cent. of saturated hydrocarbons, and 82 per cent. of nitrogen. When lead chromate was substituted for copper oxide, these difficulties were overcome.

With concentrated nitric acid in the presence of concentrated sulphuric acid, the base yields a yellow, crystalline *nitro*-compound which crystallises from aqueous alcohol in yellow needles; aqueous potassium hydroxide gives a deep red colour when added to its acetone solution. Di-*n*-butylaniline gives a green compound when heated with benzaldehyde and a small amount of zinc chloride.

Di-n-butylaniline hydrochloride was prepared by passing a stream of dry hydrogen chloride into a solution of the base in dry ether. On the addition of a further quantity of the base, an oil was precipitated which slowly solidified to clusters of colourless needles. The salt melts indefinitely at 90—105°, and solidifies on cooling to a transparent mass:

0·1095 gave 0·0875 AgCl. Cl = 19·8.

$(C_{14}H_{23}N)_2,3HCl$ requires Cl = 20·5 per cent.

This compound is very readily soluble in alcohol or chloroform, sparingly so in benzene, and insoluble in ether. It is not deliquescent.

The *picrate*, prepared in ethereal solution, crystallises from ether in yellow, rectangular plates melting at 125°. The melting point was depressed to 94—95° by the addition of picric acid.

0·1073 Gram of the picrate was dissolved in alcohol, and the solution was made up to 100 c.c. Of this solution, 5 c.c. required 12·0 c.c. of titanous chloride (1 c.c. = 0·000235 gram $C_6H_3O_7N_3$) for reduction, using Knecht and Hibbert's method.

Found: $C_6H_3O_7N_3$ = 52·6.

$C_{14}H_{23}N,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$ = 52·7 per cent.

It is readily soluble in acetone, alcohol, benzene, or chloroform, sparingly so in ether, and practically insoluble in water or light petroleum.

p-*Nitrosodi*-n-*butylaniline*.

Di-*n*-butylaniline was dissolved in an excess of dilute hydrochloric acid, the solution cooled with ice, and a solution of sodium nitrite slowly added as long as any action occurred. The deep reddish-brown solution was repeatedly extracted with ether to remove any phenyl-*n*-butylnitrosoamine which would have been formed if any monobutyl derivative had been present, and then rendered alkaline with ammonia. A green turbidity was produced, and the solution was extracted with ether. After drying the ethereal solution and evaporating the solvent, *p-nitrosodi-n-butylaniline* was obtained as a green oil:

0·1465 gave 15·3 c.c. N_2 at 20° and 745·5 mm. N = 11·94.

$C_{14}H_{22}ON_2$ requires N = 11·96 per cent.

A dilute ethereal solution of the crude *p*-nitroso-compound changes on keeping from green to a brownish-yellow colour. On passing hydrogen sulphide into an alcoholic ammoniacal solution of this compound, the solution becomes almost colourless. The reduction with zinc dust and hydrochloric acid is described later. The nitroso-compound condenses with β-naphthol in alcoholic solution to give a purplish-blue solution, which yields a precipitate on the addition of zinc chloride solution. The solution dyes chrome-mordanted wool in greenish-blue shades.

p-Nitrosodi-*n*-butylaniline condenses with gallic acid to yield a deep blue, insoluble powder. 9·7 Grams of the hydrochloride were dissolved in 75 c.c. of absolute alcohol and 3·5 grams of gallic acid added. After heating on a water-bath for two to three hours, the alcohol was distilled off, and the residue evaporated to dryness. On extracting the residue with hot water, a dark blue, insoluble powder was left, the alcoholic solution of which dyed wool a blue colour. Analysis gave N = 5·0, whereas the dibutyl homologue of gallocyanine requires N = 7·1 per cent.

p-*Nitrosodi*-n-*butylaniline Hydrochloride.*

A solution of di-*n*-butylaniline (20 grams) in a mixture of 30 c.c. of concentrated hydrochloric acid and 40 c.c. of water was cooled in a freezing mixture, and a concentrated solution of sodium nitrite added, the temperature not being allowed to rise above 5·0°. The mixture initially became pale red, then a darker red, and after passing through a succession of red shades finally almost black. When a slight excess of nitrous acid was present, the mixture was allowed to remain for two to three hours until it had attained the temperature of the room, when a mass of dark, shining crystals was deposited. The crystals were collected and purified by solution in a small amount of alcohol and precipitation with ether, the *hydrochloride* being obtained in small, greenish-yellow crystals.

0·2657 Gram of the hydrochloride was dissolved in water, the solution rendered slightly acid with hydrochloric acid and made up to 100 c.c. It was freed from air by passing in a stream of carbon dioxide. Ten c.c. were reduced by means of standard titanous chloride, using Knecht and Hibbert's method.

0·02657 Gram, in 10 c.c. of above solution, required 19·6 c.c. of $TiCl_3$ (1 c.c. = 0·000147 gram NO); NO = 10·8:

0·3340 gave 0·1773 AgCl. Cl = 13·13.

$C_{14}H_{22}ON_2,HCl$ requires NO = 11·1; Cl = 13·10 per cent.

The hydrochloride is very readily soluble in alcohol or water and insoluble in ether. An aqueous solution gives a red coloration with

ferric chloride solution, and the further addition of an excess of hydrochloric acid produces a precipitate which becomes tarry after a short time.

p-*Nitrosodi*-n-*butylaniline ferrocyanide* was obtained as a pale yellow powder by the addition of a solution of potassium ferrocyanide to a solution of the nitroso-compound in dilute hydrochloric acid. It was washed well with water, absolute alcohol, and finally with ether:

0·1987 gave 0·0346 Fe_2O_3. Fe = 12·18.

$C_{14}H_{22}ON_2,H_4Fe(CN)_6$ requires Fe = 12·40 per cent.

The compound is insoluble in water, alcohol, or ether.

The *platinichloride* is a yellow powder which, on heating, darkens about 180—190°, shrinks at 213—215°, and decomposes at a slightly higher temperature:

0·1232 gave 0·0267 Pt. Pt = 21·67.

$(C_{14}H_{22}ON_2)_2,H_2PtCl_6$ requires Pt = 22·21 per cent.

It is insoluble in ether, sparingly soluble in water, alcohol, or acetone.

The addition of alcoholic solutions of certain other metallic salts to an alcoholic solution of the nitroso-compound produced deep reddish-brown solutions. Many of these, on keeping over calcium chloride in a vacuum desiccator, deposited crystals which were either dark blue or green with a pronounced metallic lustre. They were only slowly hydrolysed by cold water, but more quickly by hot water. Acids rapidly caused hydrolysis.

The *zincichloride* forms steel-blue crystals, which dry to a red powder, melting and decomposing at 153°:

0·1263 gave 0·0623 AgCl. Cl = 12·2.

0·0571 ,, 0·0156 $ZnSO_4$. Zn = 11·1.

$(C_{14}H_{22}ON_2)_2,ZnCl_2$ requires Cl = 11·7; Zn = 10·8 per cent.

It is readily soluble in acetone or tetrachloroethane, moderately so in ethyl iodide, pyridine, or chloroform, very sparingly so in ether or benzene, and insoluble in water, carbon tetrachloride, or chloroform.

The *cadmichloride* forms stellate clusters of blue, flat prisms with a metallic lustre, which dry to a red powder. It does not melt at 260°, although at a considerably lower temperature it softens and darkens somewhat in colour:

0·1039 gave 0·0723 AgCl. Cl = 17·2.

0·0580 ,, 0·0288 $CdSO_4$. Cd = 26·8.

$C_{14}H_{22}ON_2,CdCl_2$ requires Cl = 17·0; Cd = 26·9 per cent.

It is moderately soluble in tetrachloroethane, sparingly so in absolute alcohol or acetone, and almost insoluble in benzene, ether,

light petroleum, or ethyl iodide. It dissolves in pyridine, but there was apparently some change in the compound, for the pyridine solution, on cooling, deposited a yellow solid.

The *mercurichloride* was obtained as a dark green, viscid solid by evaporating an alcoholic solution of mercuric chloride and *p*-nitrosodi-*n*-butylaniline. Benzene was added to precipitate the salt and to dissolve any excess of nitroso-compound.

After being washed several times with dry benzene, the compound was dried in a vacuum desiccator, when it was obtained as an almost black, brittle mass:

0·1373 gave 0·0827 AgCl. Cl = 14·9.

$C_{14}H_{22}ON_2,HgCl_2$ requires Cl = 14·0 per cent.

It is soluble in tetrachloroethane, acetone, nitrobenzene, chloroform, pyridine, or absolute alcohol, but practically insoluble in water, ether, benzene, or carbon tetrachloride.

The *cuprichloride* crystallises from an alcoholic solution of its components in fine, dark green needles having a decided metallic lustre, softening at 119—120°, and melting and decomposing at 123—125°. On sudden heating, it decomposes with a feeble explosion:

0·0914 gave 0·0446 AgCl. Cl = 12·1.

0·0686 „ 0·0091 CuO. Cu = 10·6.

$(C_{14}H_{22}ON_2)_2,CuCl_2$ requires Cl = 11·8; Cu = 10·5 per cent.

The compound is very readily soluble in tetrachloroethane, and moderately so in chloroform, nitrobenzene, absolute alcohol, or ethyl iodide, giving reddish-brown solutions. In pyridine it dissolves to give a green solution. It is almost insoluble in ether, benzene, carbon tetrachloride, or light petroleum.

On mixing alcoholic solutions of ferric chloride and *p*-nitrosodi-*n*-butylaniline either a pale brown powder or an almost black, amorphous compound was obtained, according to the conditions. The iron derivative apparently had a varying composition. The black precipitate gave Fe = 14·7, whilst $C_{14}H_{22}ON_2,FeCl_3$ requires Fe = 14·1 per cent. It is insoluble in ether, alcohol, or benzene, and soluble in tetrachloroethane or acetone. The brown precipitate contained Cl = 19·7.

The manganous chloride compound was obtained as a very hard, brittle mass by the evaporation in a vacuum of an alcoholic solution of its components. Stannic chloride, nickel nitrate, cobalt nitrate, or cupric nitrate also gave deep brown-coloured solutions when treated under similar conditions, whilst mercuric nitrate gave a precipitate.

Decomposition of p-*Nitrosodi*-n-*butylaniline with Alkali.*

p-Nitrosodi-*n*-butylaniline (9·4 grams) was heated under reflux for four hours with a solution of sodium hydroxide (25 grams) in 600 c.c. of water. The alkaline mixture was then distilled in a current of steam, the distillate being collected in an excess of dilute hydrochloric acid. As soon as the distillate showed absence of alkalinity, the operation was stopped, and the residue in the flask quickly cooled and filtered from tarry matter. It was neutralised by means of sulphuric acid, and extracted with ether several times. On evaporating the ethereal layer, a pale brown solid remained, which was purified by dissolving it in ammonia, passing carbon dioxide through the solution, and extracting with ether. By this means a very faint buff-coloured solid was obtained (m. p. 126—127°), which had the properties of *p*-nitrosophenol, and was characterised by means of its green potassium salt. (Found, K = 24·70. Calc., K = 24·26 per cent.) The hydrochloric acid solution in which the distillate had been collected was evaporated to dryness, leaving an almost white solid, which crystallised from absolute alcohol in white plates. It had the properties of a hydrochloride of a secondary amine and was identified as di-*n*-butylamine hydrochloride. (Found, Cl = 21·43. Calc., Cl = 21·40 per cent.) It was found that the decomposition of *p*-nitroso-*n*-butylaniline was fairly rapid, whilst in the case of the di-*n*-butyl compound the action was much slower. By using an excess of a 10 per cent. solution of sodium hydroxide and heating *p*-nitrosodi-*n*-butylaniline hydrochloride for three hours under reflux before distilling in steam, an almost theoretical yield of the dialkylamine was obtained in the form of its hydrochloride.

We have compared this method of obtaining di-*n*-butylamine with several of the methods employed for the production of the higher alkylamines, as, for example, Chancel's method (*Bull. Soc. chim.*, 1892, [iii], **7**, 405) by heating the alkyl chloride with ammonia, or Berg's method (*Ann. Chim. Phys.*, 1894, [vii], **3**, 392) by heating at 120° a mixture of the alkyl chloride, ammonia, and alcohol. By these methods it is difficult to obtain a compound free from contamination with the monoalkylamine. By the decomposition of *p*-nitrosodi-*n*-butylaniline this difficulty does not arise, and the dialkylamine hydrochloride can be readily obtained in a pure condition.

p-*Phenylenedi*-n-*butyldiamine Dihydrochloride.*

This derivative was prepared by adding an excess of zinc dust gradually to a solution of *p*-nitrosodi-*n*-butylaniline in hydro-

chloric acid. When the zinc had been added the mixture was heated for half an hour on the water-bath, by which time the solution had become almost colourless. The excess of zinc dust was collected and washed well with a small amount of warm dilute hydrochloric acid. The filtrate was treated with sodium hydroxide solution until all the precipitated zinc hydroxide had redissolved, and the separated oil was then extracted with ether. To the washed and dried ethereal solution, a solution of hydrogen chloride in *n*-butyl alcohol was added, when the dihydrochloride was precipitated as a white powder. It was collected, dried at 100°, and purified by dissolving in absolute alcohol and then adding ether, when the hydrochloride was obtained in flocculent masses of white, hair-like crystals. It separated from hot absolute alcohol in white needles:

0·1207 gave 10·25 c.c. N_2 at 18·3° and 737·8 mm. N = 9·69.
0·2284 „ 0·2236 AgCl. Cl = 24·22.
$C_{14}H_{24}N_2,2HCl$ requires N = 9·56; Cl = 24·19 per cent.

p-*Phenylenedi*-n-*butyldiamine dihydrochloride* is soluble in water or absolute alcohol, but insoluble in ether. Ferric chloride solution, when added to a neutral solution of the hydrochloride, produces a red coloration, which becomes darker and, after passing through a succession of colours, the solution is finally coloured green. The addition of a small quantity of ferric chloride solution to a solution of *p*-phenylenedi-*n*-butyldiamine dihydrochloride containing hydrogen peroxide produces initially a red colour, which changes to brown and finally becomes colourless. Bleaching powder, dilute bromine water, or neutral potassium dichromate also give a red coloration, which becomes darker, changing to purple. An excess of potassium ferrocyanide produces a red colour which is changed to green by alkalis, and pale green or blue by acids. On warming with potassium dichromate and dilute sulphuric acid or with an excess of ferric chloride, a pungent odour similar to that of *p*-benzoquinone is obtained. A bluish-green thiazine dye was prepared from an aqueous solution of the dihydrochloride by the action of potassium chromate in the presence of di-*n*-butylaniline and sodium thiosulphate. A green dye was also produced by oxidising molecular proportions of di-*n*-butylaniline and *p*-phenylenedi-*n*-butyldiamine hydrochloride. The free *base* is a liquid at the ordinary temperature.

4-*Di*-n-*butylaminobenzeneazo*-β-*naphthol*.

On diazotising *p*-phenylenedi-*n*-butyldiamine hydrochloride (1 mol.) with sodium nitrite in aqueous solution, the solution was

coloured brown and finally changed to green. The diazotised solution was freed from nitrous acid by means of carbamide and poured into an alkaline solution of β-naphthol (1 mol.). *4-Di-n-butylaminobenzeneazo-β-naphthol* was precipitated as a very dark red, insoluble powder. It crystallised from aqueous alcohol as an almost black powder having a slight metallic lustre:

0·0960 gave 9·6 c.c. N_2 at 20° and 743·5 mm. N = 11·40.

$C_{24}H_{29}ON_3$ requires N = 11·20 per cent.

Concentrated sulphuric acid dissolves this azo-compound, giving a very deep red solution. It is soluble in most organic solvents, but insoluble in water or alkalis. With aqueous platinic chloride the solution of the diazonium chloride gives a pale yellow precipitate which quickly oxidises. The acetylacetone azo-compound was obtained as an orange-yellow precipitate on adding an aqueous solution of the diazonium chloride to an alcoholic solution of acetylacetone in the presence of sodium acetate. β-Naphthylamine also combined with the diazonium chloride, giving a dark red azo-compound. With 2-naphthol-6:8-disulphonic acid ('G' acid) and 8-amino-1-naphthol-3:6-disulphonic acid ('H' acid) it gave dark red dyes.

Combination of Di-n-butylaniline with Diazotised Sulphanilic Acid.

Ten grams of sulphanilic acid were diazotised in the usual way, the solution was freed from any traces of nitrous acid by the addition of carbamide, and gradually added with continuous stirring to a solution of 10 grams of di-*n*-butylaniline in 30 grams of glacial acetic acid, following Karrer's procedure. The acetic acid solution became blood-red and a dark, oily substance separated. When all the diazo-solution had been added, the red solution was left for two hours in a shaker, at the end of which time the solution was removed and the bottle washed out with 100 c.c. of water. On rendering strongly alkaline, the sodium salt separated and was collected. For analysis a portion of the sodium salt was repeatedly extracted with hot absolute alcohol and then crystallised from aqueous alcohol (80 per cent.):

0·1399 gave 0·0239 Na_2SO_4. Na = 5·53

$C_{20}H_{26}O_3N_3SNa$ requires Na = 5·59 per cent.

Sodium 4-di-n-butylaminoazobenzene-4′-sulphonate is readily soluble in water, only sparingly so in cold aqueous alcohol (80 per cent.), but more readily so in the hot solvent.

The *potassium* salt was also prepared by adding an excess of potassium hydroxide to the red solution (potassium nitrite having

been used in the diazotisation), and purifying in the manner described above:

0·1039 gave 0·2154 CO_2 and 0·0576 H_2O. C = 56·54; H = 6·16.

0·1857 required 6·34 c.c. $N/5$-H_2SO_4 to neutralise NH_3 (Kjeldahl). N = 9·56.

0·1018 gave 0·0204 K_2SO_4. K = 9·0.

0·2571 ,, 0·1430 $BaSO_4$. S = 7·64.

$C_{20}H_{26}O_3N_3SK$ requires C = 56·16; H = 6·13; N = 9·83; S = 7·50; K = 9·15 per cent.

It crystallised from aqueous alcohol in small, orange-coloured plates, and was more easily obtained crystalline than the corresponding sodium salt, which it resembled in properties. The free azo-sulphonic acid was obtained by passing dry hydrogen chloride over the dry sodium salt. The mass became very dark red, and when the sodium salt had been completely decomposed the product was extracted several times with small amounts of absolute alcohol. On adding water and allowing to remain for some time, the acid crystallised in small, blue, shimmering cubic crystals, which did not melt at 200°. It was insoluble in benzene or ether, sparingly soluble in water, and readily so in acetone, glacial acetic acid, or absolute alcohol.

Reduction of 4-*Di*-n-*butylaminoazobenzene*-4′-*sulphonic Acid.*

The sodium salt of the azo-compound was dissolved in water, the solution acidified with hydrochloric acid, and reduced by gradually adding an excess of zinc dust. The solution became hot and soon decolorised. After heating on a steam-bath, the excess of zinc dust was filtered off and the filtrate evaporated to about half its bulk. After adding a concentrated solution of sodium hydroxide until all the precipitated zinc hydroxide had dissolved, the whole was extracted with ether, the ethereal solution dried, and a solution of dry hydrogen chloride in butyl alcohol added, when a white precipitate was formed, which proved to be identical with *p*-phenylenedi-*n*-butyldiamine dihydrochloride. (Found, Cl = 24·4. Calc., Cl = 24·2 per cent.)

Sodium 4-*Mono*-n-*butylaminoazobenzene*-4′-*sulphonate.*

To a solution of mono-*n*-butylaniline (4 grams) in glacial acetic acid (15 grams) a diazotised solution of sulphanilic acid (5 grams) was slowly added with continual stirring, following the procedure described previously. The liquid became deep brownish-red, but after shaking for four hours the colour had changed to a very deep red. The red solution was poured off, and some separated solid

matter extracted with dilute sodium hydroxide, the extract being added to the main bulk of the liquid. On rendering slightly alkaline by the addition of concentrated sodium hydroxide solution and keeping the mixture cooled in ice, a pale orange-yellow precipitate was obtained, which, after half an hour, was collected and dried. For analysis a portion was extracted with absolute alcohol several times, and finally crystallised twice from aqueous alcohol:

0·1063 gave 0·2106 CO_2 and 0·0505 H_2O. C = 54·03; H = 5·28.

0·1758 ,, 18·1 c.c. N_2 at 20·7° and 757 mm. N = 11·92.

0·1489 ,, 0·0293 Na_2SO_4. Na = 6·37.

$C_{16}H_{18}O_3N_3SNa$ requires C = 54·06; H = 5·11; N = 11·83; Na = 6·47 per cent.

The sodium derivative crystallised in small, flocculent masses, soluble in water, but sparingly so in absolute alcohol. This compound was more easily obtained crystalline than the sodium salt of dibutylaminoazobenzenesulphonic acid.

*Sodium 4-mono-*n*-butylaminoazobenzene-4'-sulphonate* was reduced by means of zinc dust and hydrochloric acid. After filtering off the excess of zinc dust and rendering strongly alkaline with sodium hydroxide solution, the solution was extracted with ether. The addition of alcoholic hydrogen chloride to the ethereal extract gave a white precipitate which crystallised from alcohol in white, shining plates, and was identified as *p*-phenylenemono-*n*-butyldiamine dihydrochloride. (Found, Cl = 29·98. Calc., Cl = 29·90 per cent.) On rendering alkaline, *p*-phenylenemono-*n*-butyldiamine was obtained on extraction with ether in white, glistening plates melting at 31° (T., 1917, **111**, 1033). After crystallisation from light petroleum, a mixture with a specimen of the base obtained by the reduction of *p*-nitroso-*n*-butylaniline melted at the same temperature.

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XV.—*Studies of Drying Oils. Part I. The Properties of some Cerium Salts obtained from Drying Oils.*

By Robert Selby Morrell.

Cerous salts of a number of organic acids have been described by Rimbach and Kilian (*Annalen*, 1909, **368**, 110), Morgan and Cahen (T., 1907, **91**, 477), Biltz (*Zeitsch. anorg. Chem.*, 1905, **45**,

89; *Annalen*, 1904, **331**, 334), and Levy ("Chemistry of the Rare Earths," 134).

The autoxidation of the cerous compounds has been investigated by Baur (*Zeitsch. anorg. Chem.*, 1897, **13**, 251; *Ber.*, 1903, **36**, 2658), Job (*Ann. Chim. Phys.*, 1900, [vii], **20**, 205), and Engler (*Ber.*, 1902, **35**, 2642), and the catalytic activity of the ceric and cerous salts has been discussed by Barbieri (*Atti R. Accad. Lincei*, 1907, [v], **15**, i, 395, 399).

In view of the large proportion of cerite earths in monazite sand it seemed advisable to investigate the properties of cerous and ceric salts of aliphatic acids of the C_{16} and C_{18} series, with special reference to their solubility in solvents and to the catalytic activity of the contained metal.

The general methods of preparation of cerous salts of organic acids are:

(1) By the action of acid on freshly precipitated cerous carbonate.

(2) By the interaction of a soluble cerous salt and the potassium salt of the corresponding acid.

The first method leads to the formation of acid salts of the type X3Ce,X, the second to the production of salts of the normal type, CeX3 (Rimbach and Kilian, *loc. cit.*) [X = acidic radicle].

In this paper the cerous salts of the following acids have been prepared and their properties investigated: palmitic, stearic, oleic, elaidic, linoleic, α- and β-elæostearic, linolenic, and abietic acids.

The method of preparation of the normal salts has been employed, and it must be pointed out that special precautions must be taken to ensure satisfactory neutralisation, otherwise the precipitated salts may be contaminated with excess of either acid or cerium.

All the salts are colourless and insoluble in water.

Cerous stearate, elaidate, β-elæostearate, and palmitate are insoluble in ether. When freshly prepared, cerous oleate, linoleate, linolenate, α-elæostearate, and abietate are readily soluble in ether or turpentine. Cerous palmitate and stearate, like the corresponding lead salts, are insoluble in turpentine.

No suitable solvents could be found from which the salts could be satisfactorily crystallised. In the case of acids forming cerous salts insoluble in ether, the granular precipitate was analysed directly, but where the salt was soluble the ethereal solution was concentrated and the solid salt obtained thereby was analysed. In all cases the salts were of the normal type CeX_3.

The ethereal solutions of the cerous salts of the unsaturated acids darken on keeping or on exposure to air and, in the case of the

linolenate, a buff-coloured precipitate having a peroxide reaction separates, corresponding with $CeO(XO_2)_2$, basic ceric oxylinolenate, and the brown ethereal solution would appear to contain a mixture of CeX_3 and CeX_4 or $CeX_3 + 5O_2 = 2CeO(XO_2)_2 + 2CeX_4$.*

Cerous oleate in ether gives, on exposure, a slight turbidity, and the solution changes only slightly towards the dark brown colour of ethereal cerous and ceric linolenates.

In an investigation of the changes which occur when drying oils are polymerised by heat (Morrell, *J. Soc. Chem. Ind.*, 1915, **34**, 105), it was pointed out that there was evidence of the shifting of intramolecular linkings prior to polymerisation.

The marked differences with regard to the insolubility in ether between cerous oleate and elaidate and cerous α- and β-elæostearates suggested that differences might be observed in the cerous salts obtained from the various thickened oils, which would give further support to the idea of change of linking.

From olive oil were obtained cerous salts of the normal type CeX_3, soluble in ether and passing only slowly into an insoluble, $CeOX_2$, type. When the olive oil is heated out of contact with the air (Morrell, *loc. cit.*), part of it (barium salt insoluble in ether or a mixture of benzene and alcohol) is of the normal type, but the barium salt soluble in a mixture of benzene and alcohol gives a soluble salt of the CeX_4 type and an insoluble basic ceric salt, $CeOX_2$. The olive oil underwent no polymerisation during the heating.

From poppy-seed oil, heated under the same conditions and containing no polymerised compound, similar cerium salts of the types CeX_4 and $CeOX_2$ were obtained. The original poppy-seed oil gave a salt of the normal CeX_3 type.

From thickened linseed oil after the removal of the polymerised substance by means of acetone the yield of basic ceric salt, $CeOX_2$, increased to nearly 50 per cent. A blank experiment with untreated linseed oil gave the normal CeX_3 and only 12·4 per cent. of a ceric salt of the $CeO(XO_2)_2$ or $CeO(XO_4)_2$ type.

The results of these experiments do not indicate conclusively that changes in linking have occurred, although full precautions were taken to avoid oxidation during the heating of the oils and in the preparation of the cerium salts. The probability of oxidation is too great to be ignored; nevertheless, in olive oil the presence of two glyceride modifications is indicated; one yielding, after heating, the normal type of cerium salt, whilst the second gives an oxidised type of cerium salt showing the existence in the oil of

* On free exposure to air, an insoluble salt of the type $CeO[XO_4]_2$ was obtained.

modifications with different properties. Applying this view to poppy-seed and linseed oil and with due consideration to chances of oxidation and formation of mixed cerium salts, there remain grounds for belief that during the thickening of poppy-seed and linseed oil changes of linking occur with the formation of modifications which on continued heating out of contact with air are polymerisable.

The properties of the cerium salts from thickened linseed oil (soluble in acetone), on the whole, resemble those from thickened poppy-seed oil, which is to be expected as the linolenic glyceride has been removed from the linseed oil by acetone after the thickening.

It seemed advisable to investigate the cause of the change in solubility without change in colour observed in certain cerium salts (for example, cerous α-elæostearate) after treatment with ether. Since the possibility of oxidation could not be decided by a cerium estimation, cerium α-elæostearate was transformed into the corresponding acid, which was examined for evidences of oxidation.

The experimental difficulties lie in the fact that China wood oil, in addition to small quantities of oleic acid and β-elæostearic acid, often contains oxidised acids, as shown by the liberation of iodine from potassium iodide: in marked contrast to linseed oil, which liberates comparatively a smaller amount of iodine.

It was found that the freshly prepared salt, readily soluble in ether, gave an acid with the melting point and high iodine value of α-elæostearic acid, but the salt, formerly soluble, and afterwards insoluble in ether, yielded a mixture of a crystalline acid melting at 45—46° and having an iodine value of 177·8, and a syrupy acid with a lower iodine value and varying iodine-liberation value.

Lead α-elæostearate was found to give 25 per cent. of a salt soluble in ether, containing an oxidised acid, and the insoluble part furnished a good yield of an acid melting at 44°.

The conclusion drawn from the experiments is that partial oxidations have occurred in spite of all precautions taken, although the cerium α-salt in ethereal solution gave no precipitate when air or oxygen was passed through it.

The occurrence of mixed unoxidised and oxidised acid in the insoluble salt can only be accounted for by the formation of an insoluble basic ceric salt of the type Ce_2X_6O (Ce = 14·1) and subsequent partial oxidation of the acid, although no decided colour change characteristic of ceric salts was observed. No appreciable amount of β-elæostearic acid was identified, so that stereoisomeric change had not occurred. If this is not admitted, then a change in the form of the cerium salt must have occurred without the pro-

duction of isomerism in the acid radicle. The evidence, on the whole, supports the theory of the formation of a basic ceric salt with subsequent partial oxidation of the acid radicle.

The rate of absorption of oxygen by cerous α-elæostearate shewed that half the amount of oxygen was absorbed in the first day, whilst more than ten days were required before the salt became approximately constant in weight.

The study of the oxygen absorption of the salt was easy to follow, and showed that with the formation of a basic ceric α-elæostearate of the type $Ce_2O(XO_2)_6$, from CeX_3 or Ce_2X_6O, one molecule of oxygen per molecule of acid was absorbed or that only one double linking was affected, so that the iodine value and the iodine-liberation value became approximately equal. It was only after a year's exposure to oxygen that the second double linking of elæostearic acid was peroxidised.

The peroxidic acid showed gradual polymerisation until the syrupy acid set to a varnish. It had all the properties of peroxidic acids described by Harries, namely, instability in the presence of alkalis, but stability towards dilute acids, and was not reduced by zinc dust and acetic acid.

The investigation of these peroxidic acids will be continued because the study of them will go far to elucidate the problem of drying oils.

Another interesting result was the indication of the presence of the β-acid among the products of oxidation of cerous α-elæostearate. β-Elæostearic acid is less easily oxidised than the α-modification, and can be separated from the mixed acids, as it is soluble in light petroleum whilst the peroxidic acid is insoluble. The yield of the acid is small, not more than 10 per cent., and, moreover, its potassium salt is comparatively stable in air. At present it must be regarded as a component of the sample of the original oil, although its cerium salt is sparingly soluble in ether and only the salt soluble in ether was employed.

The change of the α-glyceride into the β-glyceride has already been investigated (Morrell, T., 1912, **101**, 2082), and in a later communication the transformation of the α-methyl ester into the β-ester will be described.

From the results stated, the author is inclined to consider that, in drying oils, oxidation to peroxidic acids is followed by polymerisation. This polymerisation may be accelerated by other agents, which would account for a common practical use of two different driers, one essential for oxidation and the other for accelerating the subsequent polymerisation.

The oxidation of cerium α-elæostearate shows that its function as a drier can be represented by the following scheme:

$$CeX_3 \text{ or } Ce_2OX_6 \longrightarrow Ce_2(XO_2)_6$$

$$Ce_2O(XO_3)_6 + \text{drying oil} \longrightarrow CeX_3 + \begin{matrix} O\cdot CHY \\ | \\ O\cdot CHZ \end{matrix} \text{ [oxidised oil.]}$$

From evidence given before, especially under cerous linolenate, it is probable that the cerium assumes the ceric state, but it must be pointed out that the colour changes are not very marked, as would be expected if a ceric salt were formed. This may support the view of the transient nature of the ceric form.

The above representation agrees with the views of Ingle (*J. Soc. Chem. Ind.*, 1917, **36**, 318) for lead linolenate. The action of cerium salts as driers has been investigated by the author several years ago. It was found that cerium linoleate from linseed oil was a more active drier than lead linoleate, but inferior to manganese and cobalt linoleates (Mackay and Ingle, *J. Soc. Chem. Ind.*, 1917, **36**, 318).

The addition of a cerium drier to a varnish containing a lead drier does not accelerate the time of drying like a cobalt or manganese linoleate. It was observed that within a limiting value of cerium content the time of drying of a standard varnish under works conditions was independent of the mass of the cerium present.

This result is what would be expected from theory.

It is the intention of the author to investigate further the cerium salts of the acids from drying oils, and it is solely due to the pressure of war work that the results are submitted for publication in an incomplete form, but they are, in the author's opinion, of sufficient importance to justify the course taken.

Experimental.

Cerous Stearate.—This salt was prepared from pure stearic acid and pure cerous nitrate, the precipitation being carried out in neutral or slightly acid solution. It is a white, granular salt insoluble in water and very sparingly soluble in ether (0·6 per cent.) or cold turpentine; in these respects it resembles lead stearate. For analysis it was purified by means of ether:

1·0000 gave 0·1710 CeO_2. Ce = 13·91.

$(C_{18}H_{35}O_2)_3Ce$ requires Ce = 14·20 per cent.

Cerous Palmitate.—Cerous palmitate was prepared in the same manner from palmitic acid (Kahlbaum), and is a white, insoluble, granular salt. In ether its solubility is 0·8 and in turpentine 0·18

per cent. The solubility of lead palmitate in turpentine at 15° is 0·106 per cent.:

0·7544 (dried in a vacuum) gave 0·1418 CeO_2. Ce = 15·3.
0·5540 (extracted with ether) gave 0·108 CeO_2. Ce = 15·87.
$(C_{16}H_{31}O_2)_3Ce$ requires Ce = 15·36 per cent.

Cerous Oleate.—Cerous oleate (compare Morgan and Cahen, *Pharm. J.*, 1907, **78**, 428), prepared from oleic acid (Kahlbaum), is a white, granular solid which is completely soluble in ether. The ethereal solution can be kept for months in a bottle in the dark without precipitation, only a slight browning of the solution being observed:

0·8180 (dried in a vacuum) gave 0·148 CeO_2. Ce = 14·73.
0·8928 (from olive oil) gave 0·1582 CeO_2. Ce = 14·13.*
$(C_{18}H_{33}O_2)_3Ce$ requires Ce = 14·24 per cent.

The high values of cerium in the analyses are due to the slight alkalinity of the solution from which the cerium salt was precipitated.

Cerous Elaidate.—This salt is obtained in the usual manner, but it is precipitated slowly and in a more finely divided state than the oleate. Its solubility in ether is 1·07 per cent.:

0·9678 gave 0·1744 CeO_2. Ce = 14·66.
$(C_{18}H_{33}O_2)_3Ce$ requires Ce = 14·25 per cent.

Cerous Linoleate.—Linoleic acid was prepared from the corresponding tetrabromide (Rollett, *Zeitsch. physiol. Chem.*, 1909, **62**, 410). It had an iodine value of 179·6 (Wijs).

A solution of pure cerous nitrate was added to a carefully neutralised solution of linoleic acid, and the white, granular precipitated salt was analysed after being dried in a vacuum:

1·2304 gave 0·221 CeO_2. Ce = 14·62.

The salt was extracted with ether, in which it was completely soluble, and on evaporation of the filtered solution the dried salt was analysed:

0·9940 gave 0·1790 CeO_2. Ce = 14·66.
$(C_{18}H_{31}O_2)_3Ce$ requires Ce = 14·33 per cent.

Cerium α-Elaeostearate.—The salt was prepared from Chinese wood oil by saponification in the cold, neutralisation by acetic acid (cerous acetate is soluble in water), and addition of an aqueous solution of cerous nitrate.

The freshly prepared salt is completely soluble in ether, but if dried out of contact with air it is no longer soluble in that medium.

An analysis of the freshly precipitated salt (which furnished an

* A third analysis gave Ce = 14·85.

acid melting at 45—46°; I.V. = 177·8) gave the following numbers:

1·1060 gave 0·198 CeO_2. Ce = 14·64.*

$(C_{18}H_{31}O_2)_3Ce$ requires Ce = 14·34 per cent.

The salt purified by solution in ether and subsequent removal of the solvent in a current of coal gas contained Ce = 14·56, and gave an acid melting at 44—45°.

On further examination it was found to be no longer completely soluble in ether, which fact points to either oxidation during drying or to some isomeric change.

Precautions were taken to exclude oxygen during the drying, although it must be admitted that oxygen combines readily with the salt.

An analysis of a quantity of the salt which had been dried in a vacuum and kept for some time in a sealed tube in the dark showed only a slight fall in the cerium content, but 86 per cent. of the salt was found to be insoluble in ether. The slight fall in the cerium content would be accounted for by unavoidable oxidation during the drying of a larger quantity of the salt:

1·1230 gave 0·1900 CeO_2. Ce = 13·77.

The acid obtained from the cerium salt insoluble in ether was an oil [I.V. = 88 (Wijs)] liberating 28·9 per cent. of iodine, and having a molecular weight in glacial acetic acid of 411·9. It reduced Fehling's solution and restored the colour to bleached magenta solution. The slight fall in the cerium content indicates considerable modification in the acid, which would appear to have become partly oxidised and gradually polymerised to a substance, $(C_{18}H_{32}O_2,O_2)_y$.

Lead α-elaeostearate was prepared in the usual manner from cold hydrolysed wood oil.

Found: Pb = 27·12. $(C_{18}H_{31}O_2)_2Pb$ requires Pb = 27·06 per cent.

From the lead salt the corresponding acid was obtained which, on crystallisation from alcohol, melted at 48·5°. The acid liberated in two hours only 7·52 per cent. of iodine from potassium iodide in acetic acid solution. It was found that 73·4 per cent. of the original salt was insoluble in ether, and from it an acid was obtained melting at 44—45°. In its insolubility in ether lead α-elæostearate is markedly different from the cerous salt.

The portion of the soluble salt was found on recovery to be only partly soluble in the solvent, and the permanently soluble portion furnished an oily acid with an iodine value of 104 after one and a-half hours and 115 after twenty-two hours (Wijs) and liberated 36·59 per cent. of iodine after one hour.

* A second analysis gave Ce = 14·25.

The oxidation of cerium α-elæostearate will be described in detail later.

Cerous β-Elaeostearate.—β-Elæostearic acid (Morrell, T., 1912, **101**, 2082) was neutralised with the calculated quantity of potassium hydroxide and the potassium salt was dissolved in hot water (5·734 grams required 800 c.c. of hot water for complete solution). With aqueous cerium nitrate a white, granular precipitate was obtained. It is very sparingly soluble in ether or other organic solvents with the exception of hot benzene, from which it can be obtained as a white powder on evaporation of the solvent. The salt can be dried in a vacuum at 110° without loss in weight:

1·0436 gave 0·1526 CeO_2. Ce = 14·25.

$(C_{18}H_{31}O_2)_3Ce$ requires Ce = 14·34 per cent.

It must be pointed out that special precautions must be taken in the precipitation of the salt so as to ensure a neutral solution. Unless care be taken, the cerium content in the precipitated salt may fall to 13·6.

After recrystallisation from acetone, β-elæostearic acid showed an iodine-liberation value of 0·8 per cent. of iodine (two hours). On exposure in the dark in dry air for a fortnight it gained nothing in weight, although there was a faint, rancid odour, but no change in colour. In the light the gain in weight after a month was 2·3 per cent. The potassium salt of the β-acid, on exposure to air in fourteen days, gained only 0·22 per cent. in weight, and after a month's exposure in light the gain in weight was 1·22 per cent., although the salt had become slightly yellow.

Cerous Linolenate.—Kahlbaum's linolenic acid (iodine value, 276—279) and pure cerous chloride were used for the preparation of the salt. Cerous linolenate is a white, granular solid which is completely soluble in ether. The ethereal solution was evaporated in a coal-gas atmosphere and the salt dried in a vacuum. It did not show as great a tendency to pass into an insoluble form as in the case of cerous α-elæostearate, and the salt can be kept for a month in a sealed tube without losing its power of dissolving in ether:

0·8098 gave 0·1480 CeO_2. Ce = 14·7.

$(C_{18}H_{23}O_2)_3Ce$ requires Ce = 14·42 per cent.

The ethereal solution of the salt gradually darkens in colour when exposed to light and a brownish-buff-coloured precipitate is formed, which liberates iodine from potassium iodide in dilute acetic acid solution. It is presumably a basic ceric salt of an oxylinolenic acid:

0·0804 gave 0·0184 CeO_2. Ce = 18·63.

$CeO(C_{18}H_{29}O_2)_2$ requires Ce = 19·7 per cent.

$CeO(C_{18}H_{29}O_2,O_2)_2$ requires Ce = 18·10 per cent.

On free exposure to air, the ethereal solution deposited a salt [Ce=17·0]. $CeO(C_{18}H_{29}O_2,O_4)_2$ requires Ce=16·7, and $CeO(C_{18}H_{29}O_2,3O)$ requires Ce=17·3 per cent. The brown-coloured ethereal solution contained a cerium salt:

0·9356 gave 0·1484 CeO_2. Ce=12·91.

Most probably the brown ethereal solution contained a mixture of ceric and cerous salts of the types CeX_4 (Ce=11·2) and CeX_3 (Ce=14·4), rather than a basic ceric oxylinolenate of the type $Ce_2O(XO_2)_6$ (Ce=13·0 per cent.). The proportion of oxidised insoluble salt to oxidised soluble salt was 1:5·2.

The change of colour to a yellow or brown shade is noticeable when solutions of cerous salts in organic solvents are exposed to the air.

Reference will be made to the other basic salts in the examination of ceric salts from drying oils.

Cerous Abietate.—Abietic acid was prepared from French rosin by repeated recrystallisation from 70—90 per cent. alcohol. On the ninth crystallisation an acid was obtained melting at 150—156°. The white cerous abietate dissolves in ether to the extent of 97·8 per cent., is soluble in turpentine, and does not lose weight at 100—110°:

0·9772 gave 0·163 CeO_2. Ce=13·62.

$(C_{20}H_{29}O_2)_3Ce$ requires Ce=13·43 per cent.

The cerium salt prepared from crude American resin was not completely soluble in ether (15·44 per cent. was insoluble), and it contained only 10·2 per cent. of cerium owing to the presence of abietic anhydride. The cerium salt soluble in ether contained Ce=7·83 per cent.

An ethereal solution of cerous abietate gradually becomes orange and a precipitate is formed, similar to the behaviour of cerous linolenate in ether.

Cerous Salts from Thickened Drying Oils.

Olive Oil.—After the saponification of olive oil, the lead salt soluble in ether was transformed into the barium salt, which was treated with a mixture of benzene and alcohol, whereby 25·9 per cent. dissolved (Morrell, *loc. cit.*). It may be pointed out that 47·8 per cent. of the barium salt soluble in a mixture of benzene and alcohol is soluble in ether.

The cerous salt from the soluble barium salt gave the following result on analysis:

0·8928 gave 0·1582 CeO_2. Ce=14·13.

$(C_{18}H_{33}O_2)_3Ce$ requires Ce=14·24 per cent.

The salt of the CX_3 or normal type is soluble in ether, although on exposure to air it becomes only partly soluble, leaving a residue (30·86 per cent. of the whole), which contains Ce=20·15 and is evidently basic ceric oleate.

$CeO(C_{18}H_{33}O_2)_2$ requires Ce=19·5 per cent.

The cerium salt from the insoluble barium salt is likewise of the normal type.

From the thickened olive oil (Morrell, *loc. cit.*) the barium salt, insoluble in a mixture of benzene and alcohol and insoluble in ether, gave a cerous salt of the normal type soluble in ether:

0·9964 gave 0·166 CeO_2. Ce=14·03.

This salt could be completely redissolved in ether.

On the other hand, the cerium salt from the barium salt (37·2 per cent.) soluble in a mixture of benzene and alcohol was of two types, namely, one soft and viscous, soluble to the extent of 68·45 per cent. in ether and containing Ce=11·62, whereas a salt of the CeX_4 type requires Ce=11·07 per cent., and the other of the basic ceric type $CeOX_2$ containing Ce=19·9 (Calc., Ce=19·5 per cent.).

Thickened Poppy-seed Oil.

The cerous salts of the raw poppy-seed oil are of the normal type, CeX_3, and soluble in ether to the extent of 93 per cent. When poppy-seed oil is thickened (Morrell, *loc. cit.*), two types of cerium salts are obtained from the oil soluble in acetone, namely, CeX_4 (65 per cent.), containing Ce=11·36 per cent. and soluble in ether, and $CeOX_2$ (25 per cent.), containing Ce=20·9 per cent. and insoluble in ether.

From the iodine values of the acids obtained directly from the thickened oil, there is no evidence that oxidation has occurred during heating, but the acid obtained from the cerium salt of the CeX_4 type has an iodine value of 71—79, indicating that oxidation of the cerium had taken place, presumably during the handling of the salt, and it is possible that the salts of the CeX_4 and $CeOX_2$ types may contain partly oxidised X-groups, which would explain the low iodine value given above.

Thickened Linseed Oil.

Ordinary linseed oil was transformed into the lead salt soluble in ether, and from it into barium salts, which were extracted with a warm mixture of benzene and alcohol; of these, 82·5 per cent. consisted of the normal CeX_3 type [soluble in ether, but not completely soluble in that solvent on careful recovery], and the in-

soluble residue showed ceric properties, with 12·4 per cent. of the $CeO(XO_2)_2$ or $CeO(XO_4)_2$ types.

When linseed oil is thickened by heating under the conditions previously referred to, the mixture of cerium salts obtained from the non-polymerised part soluble in acetone is soluble in ether only to the extent of 50 per cent., and consists essentially of salts of the CeX_4 and $CeOX_2$ types (see above). It is difficult to avoid completely chances of oxidation during the thickening of the oil and the handling of the cerium salts, but the results seem to indicate the production of modifications of the oil on heating, which are prone to oxidation, and this view is not contrary to experience with thickened oils as drying oils.

The Oxidation of Cerous α-Elaeostearate.

The absorption of dry oxygen by cerous α-elæostearate, soluble in ether, and recovered from that solvent, was determined by:

(*A*) Direct measurement of the volume of oxygen absorbed.

(*B*) Increase in weight of cerous salt.

(*A*) 0·268 Gram of cerous α-elæostearate, soluble in ether, was kept in contact with a known volume of pure dry oxygen and the diminution in volume observed.

Percentage Weight of Oxygen Absorbed.

In 16 hours at room temperature.....	4·4
„ 24 „ „ „	8·7
„ 3 „ „ „	9·37
„ 4 „ „ „	9·79

$Ce_2O(C_{18}H_{31}O_2,O_2)_6$ requires 9·66 per cent.
$Ce_2(C_{18}H_{31}O_2,O)_2$ requires 9·8 per cent.

In 4$\frac{2}{3}$ days at room temperature	10·0
„ 6$\frac{2}{3}$ „ „ „	10·8
„ 7$\frac{2}{3}$ „ „ „	11·19
„ 16$\frac{2}{3}$ „ „ „	12·54
„ 65 „ „ „	17·43
„ 10 months „ „	19·01

$Ce(C_{18}H_{31}O_2,O_4)_3$ requires 19·65 per cent.
$Ce_2O(C_{18}H_{31}O_2,O_4)_6$ requires 19·3 per cent.

After ten months, the salt gave the following results on analysis: 0·281 gave 0·042 CeO_2. Ce = 12·1.

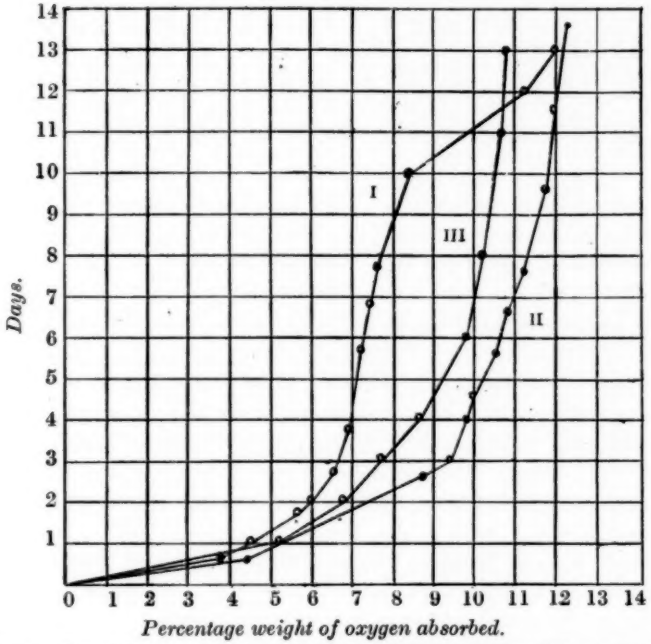
$C_{18}H_{31}O_2,O_4)_3Ce$ requires Ce = 11·97 per cent.
$(C_{18}H_{31}O_2,O_4)_3CeO$ requires Ce = 11·81 per cent.

(*B*) Quantities of about 20 grams of the salt, purified by ether, were kept in dry oxygen and the gain in weight of the salt was determined from time to time.

			Per cent.	
19·243 Grams showed a gain in weight in	1 day	=	6·82	5·27
	3 days	=	—	7·7
(Average temperature 120°)	4 „	=	8·65	—
	6 „	=	9·8	9·6
	8 „	=	10·24	—
	11 „	=	10·66	10·4
	13 „	=	10·9	0·6

During the first eight hours, the rise in temperature of the salt was very decided, and after five hours the difference in tempera-

Absorption of Oxygen by Cerium Elaeostearate.



Curves I and II were obtained from the volume changes of the oxygen. Curve III shows the percentage increase in weight of the salt.

ture between the salt and the air in the room was as great as 11·5°; at the end of eight hours the difference was 3·5°.

The relations between time and absorption are shown in the curves. In curve I, after the tenth day, the salt was repowdered and the oxygen renewed.

The cerium salt, in ethereal solution, was transformed into the acid by means of dilute sulphuric acid, whereby a viscous oil of slight rancid odour was obtained. It was extracted by light petroleum, in which 4 to 14 per cent. was soluble. The part soluble in light petroleum was a syrup, from which crystals melting at 67—68° were obtained. These were presumably β-elæostearic acid.

The syrupy mother liquor had strong reducing and peroxidic properties, and was probably of an aldehydic or aldehydo-acidic character. The residue insoluble in light petroleum was a viscous solid with strong peroxidic properties, which were destroyed on warming the substance with mineral acids or alkalis, but were retained in the presence of 10 per cent. acetic acid. On warming with dilute sulphuric acid and testing with titanium dioxide, a definite peroxidic reaction was obtained:

0·1544 gave 0·3878 CO_2 and 0·1328 H_2O. C = 68·5; H = 9·56.
0·1370 „ 0·340 CO_2 and 0·1124 H_2O. C = 68·48; H = 9·11.

Iodine value = 79·35; iodine liberated in two hours = 50 per cent. O = 6·3; in twenty hours = 73·63 per cent. O = 9·3.

$C_{18}H_{32}O_4$ requires C = 69·23; H = 10·25 per cent. Iodine value = 81·4. O = 10·3 per cent. Iodine liberated = 81·6 per cent.

$C_{18}H_{32}O_5$ requires C = 66·00. H = 9·7 per cent. Iodine value = 73·4.

The viscous mass undergoes slow polymerisation, and the molecular weight increases when the substances is kept in a vacuum, so that it eventually hardens to a varnish-like mass. In glacial acetic acid (after fourteen days in a vacuum), M.W. = 484—518.

After twenty-eight days in a vacuum, M.W. = 518—535.

After two months in a vacuum, M.W. = 654—691.

$C_{18}H_{32}O_4$ requires M.W. = 312.

The peroxidic acid was boiled with freshly prepared calcium carbonate and water under reflux for three hours, and then extracted with ether. The ethereal extract (14·7 per cent.) was a syrup reducing Fehling's solution and having the usual peroxidic properties.

The red, viscous residue, which likewise reduced Fehling's solution, liberated iodine from potassium iodide and gave a hydrogen peroxide reaction with titanic oxide. It yielded a series of viscous salts with soluble barium, cadmium, cobalt, copper, and strontium compounds, and in slightly ammoniacal solution, a granular, basic lead salt of the peroxidic acid:

1·4586 gave 0·8238 $PbSO_4$. Pb = 38·61.

$C_{18}H_{31}O_2,O_2,PbOH$ requires Pb = 38·69 per cent.

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MANDER BROTHERS,
WOLVERHAMPTON. [*Received, December 11th*, 1917.]

XVI.—*The Colouring Matters of Camwood, Barwood, and Sanderswood.*

By Pauline O'Neill and Arthur George Perkin.

Of the four well-known "insoluble" red dye-woods, sanderswood, barwood, caliaturwood, and camwood,* the first-named has been most closely examined, and although barwood and caliaturwood have received some attention, no description of the colouring matter of camwood appears to be on record. The close similarity in the dyeing properties of these woods, and the fact that all are substantive to wool, suggests that the dyes present are chemically allied, and it is indeed conceivable from the very similar shades given by sanderswood, barwood, and caliaturwood that the same colouring matter may be present in each case. Camwood, on the other hand, gives with mordanted wool somewhat bluer tones,

	Chromium.	Aluminium.	Tin.	Iron.
Camwood	Reddish-violet	Red	Bluish-red	Violet
Sanderswood	Brownish-red	Orange-red	Red	Maroon

and its colouring matter, according to dyers, is more readily dissolved by water than that of the other dye-woods of this class. A chemical comparison of this with the santalin of sanderswood appeared desirable, the latter having somewhat recently been closely studied by Cain and Simonsen (T., 1912, **101**, 1061). These authors have suggested for santalin the formula $C_{15}H_{14}O_5$, also considered probable by Weyermann and Haffely (*Annalen*, 1850, **74**, 226), and find that this may be expressed as

$$C_{14}H_9O_2(OH)_2(OMe).$$

Of the numerous derivatives of this colouring matter described in their paper, santalin dimethyl ether, $C_{14}H_9O_2(OMe)_3$, is specially interesting in that, by oxidation, veratric, anisic, and butyric acids can be prepared from it. That sanderswood contains, in addition to santalin, a second colouring matter appears possible from the work of Weidel (*Zeitsch. für Chem.*, 1870, **6**, 83), who obtained from it, in addition to his colourless, crystalline santal, $C_8H_6O_3$, a bright red substance, $C_{14}H_{12}O_4$, soluble in alkaline solutions with a purplish-red colour. Curiously enough, in the more recent accounts of sanderswood, this paper appears to have been lost sight of.

The present investigation, although commenced a considerable

* A less known insoluble red wood is the Narra wood of the Philippine Islands, *Pterocarpus*, spp., which has been investigated by Brooks (*loc. cit.*).

time ago, is of necessity somewhat incomplete, and must remain so for the present, on account of other work which in the present circumstances is of greater importance.

Experimental.

In order to obtain some idea as to the solvent properties of the constituents of camwood, the fractional extraction of a few grams of the powdered wood in a Soxhlet apparatus was first carried out, and for the sake of comparison, samples of barwood and sanderswood were similarly treated. Employing in the order given, benzene, ether, ethyl acetate, acetone, and alcohol, fractions very similar in appearance were obtained from each of these woods, as if, indeed, all contained the same constituents. From the behaviour of the solvents, however, it became apparent that more than one colouring matter was present, for, after the removal of colourless substances by means of benzene, ether somewhat slowly dissolved a red colouring matter, and when this ceased to pass into solution, a considerable amount of a brownish-red substance, evidently the main product, was extracted by means of commercial ethyl acetate. Subsequently, by means of acetone, a small amount of a similar compound was isolated, whereas the final alcoholic extract contained traces of a darker and somewhat uninviting-looking product.*

In working with camwood on the larger scale, such a process was impracticable, and an alcoholic extract was first prepared. In order to isolate the mixed colouring matters, the precipitation of these as lead salts by means of lead acetate according to Meier's method (*Arch. Pharm.*, 1848, **55**, 285) was at first adopted, but the subsequent filtration processes were so extremely tedious that a more rapid method was devised. This consisted in the addition of concentrated barium hydroxide solution to the wood extract in boiling 80 per cent. alcohol, there being thus formed a precipitate of the barium salt, which filtered rapidly, and was subsequently washed with 80 per cent., and finally with boiling alcohol. The reddish-brown precipitate suspended in water was decomposed by means of dilute hydrochloric acid, the crude colouring matter collected, and, in order to remove as far as possible obstinately retained mineral matter, boiled two or three times with 5 per cent. hydrochloric acid solution. When cold, the product was repeatedly ground with water to decompose completely the oxonium hydrochloride present.

* By exhaustion with alcohol, camwood gave 16 per cent. and sanderswood 19·4 per cent. of extract.

The dried substance was now dissolved in a little alcohol, the solution stirred with purified sand, the alcohol removed by evaporation, the residue finely ground, and extracted in a large Soxhlet apparatus with commercial ethyl acetate. At the end of the operation some quantity of the colouring matter had separated out (*A*), and from this the supernatant liquid was decanted, evaporated to a small bulk, and poured into ether, causing the deposition of some quantity of brown precipitate, which was added to *A*. That fraction soluble in ether is referred to later as *B*.

A was dissolved in absolute alcohol, the solution treated at about 60° with alcoholic potassium acetate solution, and the voluminous precipitate of the potassium salt collected and washed with alcohol (compare Cain and Simonsen, *loc. cit.*). It was decomposed in warm aqueous suspension with dilute sulphuric acid, the reddish-brown product, after washing, allowed to dry on porous porcelain, dissolved in a little alcohol, and reprecipitated by pouring into ether. Finally, it was digested with boiling purified ethyl acetate, which removed a trace of more readily soluble substance, and repeatedly washed with the same solvent.

Found: C = 65·68, 65·49; H = 5·47, 5·52.

$C_{15}H_{14}O_5$ requires C = 65·69; H = 5·11 per cent.

This substance, for which the name iso*santalin* is proposed, consists of a dark chocolate-coloured powder which on grinding becomes redder in appearance. As deposited from dilute alcohol, it could not be obtained in a definitely crystalline condition, and although when isolated from ethyl acetate the product frequently exhibited minute serrated edges, detached crystals have as yet not been observed. When heated, it showed no signs of melting, had darkened at 280°, and was fully decomposed at 290—300°, being then a carbonaceous powder. It is readily soluble in boiling methylated spirit, but with hot absolute alcohol, it resinifies and does not readily pass into solution. The general properties of this substance are described later in comparison with those of santalin.

Although the elementary analysis of *iso*santalin was in agreement with the formula $C_{15}H_{14}O_5$ proposed for santalin by Cain and Simonsen, Zeisel determinations* of the former showed that it could not possess this formula, which would require, as determined by these authors, $CH_3 = 5·47$ per cent. Indeed, the best expression for the figures obtained is given below, as the result of the analysis of numerous preparations dried at 160°.

* These were carried out by Perkin's method, with and without acetic anhydride, and employing as a precaution bulbs containing a suspension of amorphous phosphorus.

Found: CH_3=6·82, 7·01, 7·03, 6·85, 7·30.

$C_{22}H_{16}O_5(O{\cdot}CH_3)_2$ requires C=65·75; H=5·02; CH_3=6·85 per cent.

The potassium salt, prepared with boiling alcoholic potassium acetate, was repeatedly washed with alcohol, and consisted of an amorphous, reddish-brown powder. In case the *iso*santalin is impure, the precipitate is not granular at this temperature, but congeals to resinous lumps.

Found: K=2·71, 3·03, 3·08, 3·06, 2·26.

$(C_{24}H_{21}O_8K)(C_{24}H_{22}O_8)_3$ requires K=2·18 per cent.

$C_{72}H_{65}O_{24}$ requires K=2·88 per cent.

These figures were again distinct from those obtained by others for the potassium salt of santalin, $C_{30}H_{27}O_5K$, which requires K=6·76 per cent.

To decide between the two formulæ given above is not easy, for although the latter agrees best with the analyses obtained, *iso*santalin obstinately retains traces of ash which naturally accumulate in the precipitate, and, again, this amorphous potassium salt is not easy to wash. When an alcoholic solution of *iso*santalin is treated with a mineral acid, an intense reddish-violet solution is obtained, which is evidently due to the formation of an oxonium salt. These compounds, owing to their ready solubility in alcohol and acetic acid, could not be satisfactorily isolated, although the hydrobromide, which is fairly stable, can be obtained on evaporating its alcoholic solution as a black, glassy mass. They are also produced to some extent in the insoluble form by the action of hot dilute aqueous acid, and are gradually decomposed in contact with water, with regeneration of the reddish-brown colour of the original dye.

Acetyl Derivative.—The substance was digested with boiling acetic anhydride and a trace of pyridine for three hours, and the solution poured into water. The precipitated product when dry was dissolved in benzene, the solution filtered if necessary, and poured into light petroleum. The deep salmon-coloured powder was finally washed with a little ether.

Found: C=63·54; H=4·95.

$C_{24}H_{18}O_8(C_2H_3O)_4$ requires C=63·36; H=4·95 per cent.

An acetyl determination by the ethyl acetate method gave $C_2H_4O_2$=39·67, whereas the above formula requires $C_2H_4O_2$=39·60 per cent. These figures are very similar to those found by Cain and Simonsen for acetylsantalin.

It did not possess a definite melting point, but gradually decomposed without fusion between 250° and 280°, forming a carbon-

aceous powder. It was readily soluble in benzene, sparingly so in alcohol, and has not been obtained as yet in a definitely crystalline condition.

A molecular weight determination, employing naphthalene as solvent, gave the following result:

0·633 in 13·5 naphthalene gave $\Delta t = -0·14°$. M.W. = 2344.

This small depression did not appear to arise from a separation of the substance during the crystallisation of the naphthalene. The result is interesting, as it approximates to the formula $[C_{24}H_{18}O_7(C_2H_3O)_4]_4$, M.W. = 2360, which accords with the formation of the potassium salt, $C_{96}H_{87}O_{32}K$, previously referred to. Whereas the substance on the one hand may be regarded as itself highly associated, it is quite probable that the association occurs in the solution of naphthalene or that a colloidal solution is thus produced. Complex salts, again, of the character of potassium *iso*santalin can be obtained from simple substances, such as gallacetophenone (T., 1903, **83**, 131), which with aqueous potassium acetate forms potassium trigallacetophenone, $C_{24}H_{29}O_{12}K$.

Examination of the Fraction B.

Whereas *iso*santalin is almost entirely precipitated when its concentrated alcoholic solution is poured into ether, a second colouring matter is present which in these circumstances remains dissolved. The residue obtained by evaporation of the extract gave C = 66·54, H = 5·61, CH_3 = 8·06 per cent., figures indicating in the light of later results the presence of *iso*santalin and a third substance of high methoxy-content as impurities. With the object of removing the former, a concentrated alcoholic solution was poured into much benzene, the resinous precipitate, which separated in small quantity, removed, and the highly fluorescent liquid gradually evaporated. Any deposit which quickly separated was neglected, the clear liquid concentrated until bright red flocks separated, and these were collected and washed with benzene.

A more rapid method of isolating this substance, although in a cruder form, was to pour a concentrated alcoholic extract of the wood into boiling benzene, and to submit the liquid to fractional evaporation. The product could be obtained purer by a second treatment in the same manner. The bright scarlet powder obtained by these methods gave CH_3 = 8·10 per cent., a figure showing no reasonable connexion with *iso*santalin, and further purification was evidently necessary. This was effected by treating a concentrated solution of the colouring matter in alcohol with

a little hydrobromic acid, and repeatedly shaking the liquid with ether, in which the hydrobromide is insoluble.* The solution of the latter was now poured into water, and in order completely to remove hydrobromic acid, the mixture was gently warmed with sodium acetate solution. Finally, the compound thus isolated was dried on sand, extracted with ether, the liquid diluted with a little benzene, and the red deposit which separated during evaporation washed with benzene.

Found: C = 67·63; H = 5·33; CH_3 = 7·13, 7·42.

$C_{24}H_{24}O_7$ requires C = 67·92; H = 5·65; CH_3 = 7·08 per cent.

Such a formula, which represents this compound as *iso*santalin less one atom of oxygen, but richer in hydrogen, suggests the replacement of a CO-grouping in the latter by CH_2, but as this for the present must remain hypothetical, the compound will be tentatively referred to as *deoxy*iso*santalin*.

It consists of a scarlet, amorphous powder which has not yet been obtained in a definitely crystalline condition. When heated, the preparation did not show any well-defined melting point, but decomposed at 160—165° with the evolution of gas. It is readily soluble in pure ethyl acetate, sparingly so in ether, and is again distinguished from *iso*santalin by the redder shades it gives on dyeing and the redder tone of its alkaline solutions. A fuller account of these is given later. When a solution of the substance in absolute alcohol is treated with potassium acetate, no immediate precipitation of potassium salt occurs as happens in the case of *iso*santalin, and only when excess of the reagent is employed is a gelatinous deposit formed. The presence of this is no doubt responsible for the resinous condition of impure potassium santalin when this is prepared in the presence of boiling alcohol. It was acetylated by boiling with acetic anhydride and pyridine, and the product, isolated by means of water, was dissolved in benzene, precipitated by light petroleum, and subsequently washed with pure ether.

Found: C = 64·34, 64·61; H = 5·40, 5·29; $C_2H_4O_2$ = 39·67, 39·94.

$C_{24}H_{20}O_7(C_2H_3O)_4$ requires C = 64·86; H = 5·40; $C_2H_4O_2$ = 40·53 per cent.

*Acetyldeoxy*iso*santalin* thus contains the same number of acetyl groups as acetyl*iso*santalin. It consists, when dry, of an almost colourless powder, differing considerably in appearance from acetyl-*iso*santalin, and is also more readily soluble in benzene. When heated, it fused and decomposed at 170—175°:

* The ethereal liquid contained some quantity of an almost colourless phenolic substance which did not appear to be readily susceptible of crystallisation.

0·7485 in 12·13 naphthalene gave $\Delta t = -0·325°$. M.W. = 1324.
$(C_{32}H_{32}O_{11})_2$ requires M.W. = 1184.

Acetyldeoxy*iso*santalin in these circumstances thus shows approximately one-half the molecular weight of acetyl*iso*santalin, a property again distinguishing these two substances.

Sanderswood.

Although *iso*santalin closely resembled in its general reactions the santalin of sanderswood, the formula $C_{15}H_8O_3(O·CH_3)_2$ assigned to the latter by earlier workers nevertheless pointed to a considerable difference between the two substancs. For purposes of comparison, an alcoholic solution of sanderswood was prepared, the colouring matter isolated by means both of lead acetate and baryta, and the product worked up by identical methods to those previously employed with camwood. As a result, it was found that the phenolic constituents of both woods closely resembled one another in general properties, and two distinct compounds, santalin and deoxysantalin, corresponding with *iso*- and deoxy*iso*-santalin, were isolated. The santalin was finally purified by extraction with purified ethyl acetate, and could be subsequently crystallised from dilute alcohol.

Found: C = 65·70; H = 4·90; CH_3 = 6·81, 7·09.
$C_{15}H_{14}O_5$ requires C = 65·7; H = 5·11; CH_3 = 5·47 per cent.
$C_{24}H_{22}O_8$,, C = 65·8; H = 5·02; CH_3 = 6·85 per cent.

Santalin is therefore isomeric with *iso*santalin, and cannot possess the formula $C_{15}H_{14}O_5$. It consisted of a chocolate-coloured powder, very similar in appearance to *iso*santalin, readily soluble in hot methylated spirit, although with absolute alcohol it resinified and dissolved with difficulty. When heated, it commenced to soften at 243°, decomposed at 250—260°, and at 270° had become a honeycombed, carbonaceous mass. Cain and Simonsen (*loc. cit.*) describe santalin as melting at 223—226°, but from the examination of the colouring matter isolated according to their direction and in other ways, it seemed certain that santalin decomposes at about the temperature stated above, and does not possess a distinct melting point. The decomposition of this substance, however, occurs at a much lower temperature than in the case of *iso*santalin. It was first pointed out by one of us (T., 1899, **75**, 443) that the commercial santalin of Merck yielded with alcoholic potassium acetate a maroon-coloured salt, which on analysis gave K = 6·94, corresponding with the formula $C_{30}H_{27}O_{10}K$. Although in this case, as was indeed indicated, the reaction was

only given as a general illustration of the potassium acetate method, this result appeared to be correct, for not only was it confirmed by Cain and Simonsen, but Brooks again (*Philippine J. Sci.*, 1910, **5**, 448) obtained from narrin an allied colouring matter of narra wood, *Pterocarpus*, spp., a copper salt, $(C_{15}H_{13}O_5)_2Cu$. Experiments now carried out with pure santalin gave a very different result, the potassium salt prepared by means of boiling potassium acetate giving K=2·45 per cent., a figure very similar to that yielded by potassium *iso*santalin.

There was some reason to suspect that the commercial santalin sample just referred to represented the precipitate derived by acidification of an alkaline extract of the wood, and as it is known that in this way some alteration of the colouring matter, or at least a portion of it, occurs, it was interesting to examine the potassium salt obtained from this crude material. Such a preparation, although very thoroughly washed, contained free mineral matter, and the potassium salt derived from it gave K=4·01 per cent. This result, although higher than that given by pure santalin, is not sufficiently so to explain the analysis of the original product, which would thus appear to have contained much free mineral matter.

The potassium salt of santalin may thus be represented, as in the case of the *iso*santalin compound, as either $C_{72}H_{65}O_{24}K$ or $C_{96}H_{87}O_{32}K$.

Santalin in alcoholic solution shows evidence of the formation of soluble oxonium salts with mineral acids, and although it closely resembles *iso*santalin, gives colour reactions which indicate that it is not the same substance.

	Santalin.	iso*Santalin.*
Alcoholic hydrobromic acid	Crimson	Reddish-violet
Dilute sodium hydroxide	Dull red	Dull violet
Alcoholic ferric chloride.....	Violet	Bluish-violet

Again, the solution of *iso*santalin in alcohol is much browner than that of santalin. Somewhat more marked are the differences in shade given by these colouring matters in similar circumstances, especially when mordants are employed. For dyeing the colouring matter, 0·25 gram in alcoholic solution was added to the water in the dye-bath, and the dyeings were carried out (*a*) employing wool alone, (*b*) employing wool alone and subsequently saddening with bichrome, (*c*) employing wool mordanted with bichrome and cream of tartar, and (*d*) employing wool mordanted with bichrome and sulphuric acid. The results obtained were as follows:

	(*a*)	(*b*)	(*c*)	(*d*)
Santalin ...	Pale dull red	Dull reddish-brown	Pale reddish-pink	Pale reddish-pink
*iso*Santalin	Pale violet-red	Dull violet-maroon	Violet-red	Violet-red, weaker than (*c*).

Acetylsantalin, prepared in the same way as acetyl*iso*santalin, closely resembled the latter in appearance.

Found: $C_2H_4O_2 = 39{\cdot}58$, $38{\cdot}96$.

$C_{24}H_{18}O_8(C_2H_3O)_4$ requires $C_2H_4O_2 = 39{\cdot}6$ per cent.

It consisted of a deep salmon-coloured powder, which commenced to decompose at about 225°, and at 255—260° swelled up to form a carbonaceous mass:

0·7258 in 12·03 naphthalene gave $\Delta t = -0{\cdot}165°$. M.W. = 2558.

The small depression thus obtained is similar to that given by acetyl*iso*santalin, and approximates to the formula $(C_{32}H_{30}O_{12})_4$.

Deoxysantalin.

Sanderswood resembles camwood in containing a second, more readily soluble colouring matter, for which the name *deoxysantalin* is suggested. It may be prepared according to the method given for the isolation of deoxy*iso*santalin.

Found: C = 67·59, 68·10; H = 5·08, 5·70; $CH_3 = 7{\cdot}21$.

$C_{24}H_{24}O_7$ requires C = 67·92; H = 5·65; $CH_3 = 7{\cdot}08$ per cent.

It consists of a bright red powder, the ethereal solution of which possesses a greenish fluorescence, but it has not yet been obtained in a crystalline condition. Alcoholic potassium acetate gives no immediate precipitate of potassium salt, but after some time or by means of excess of the reagent a gelatinous deposit separates. A comparison of the colour reaction of deoxysantalin (*a*) and deoxy-*iso*santalin (*b*) are given in the following table. These, compared respectively with santalin and *iso*santalin (see earlier), possess much yellower tones.

	(*a*)	(*b*)
Alcoholic solution	Orange-brown	Orange
Alcoholic hydrobromic acid	Scarlet	Bright crimson
Dilute sodium hydroxide	Scarlet	Crimson-scarlet
Alcoholic ferric chloride.....	Maroon	Violet

The dyeing experiments were carried out by the processes which were adopted with santalin and *iso*santalin.

	(*a*)	(*b*)	(*c*)	(*d*)
Deoxysantalin...	Red	Dull bluish-red	Dull crimson	Red
Deoxy*iso*santalin	Pale reddish-violet	Red-puce	Dull reddish-violet	Pale dull reddish-violet

As a result, it was found that although in general character the shades given by santalin and deoxysantalin are similar, the latter is by far the better dye, possessing a stronger and brighter appearance. The difference between *iso*santalin and deoxy*iso*santalin in this respect was not so marked, and, if anything, was in favour of the former.

Acetyldeoxysantalin was obtained as an almost colourless amorphous powder, readily soluble in benzene.

Found: C = 64·43; H = 5·50; $C_2H_4O_2$ = 39·30.
$C_{24}H_{20}O_7(C_2H_3O)_4$ requires C = 64·86; H = 4·50; $C_2H_4O_2$ = 40·52 per cent.

Deoxysantalin is thus isomeric with deoxy*iso*santalin.

The first isolation of a colouring matter from sanderswood was carried out by Meier (*loc. cit.*), who employed ether as a solvent, and describes this as red, microscopic prisms melting at 104—105°, but did not analyse his product. A repetition of Meier's process failed to give the substance in a crystalline condition, as, indeed, Weyermann and Haffely (*loc. cit.*) found, but the product was interesting in that it evidently consisted mainly of deoxysantalin, being bright red and giving no immediate precipitate with alcoholic potassium acetate. This was not to be wondered at, as pure santalin is not soluble in pure ether.

In the hope of obtaining the colouring matter in a crystalline form, wool was dyed with sanderswood in the usual manner, and attempts were made to extract it by means of solvents from the fibre, but without success. Although the exact reason for its insolubility was not determined, it seems likely that it is there fixed as an acid calcium salt, because only by steeping the dyed material in 33 per cent. hydrochloric acid overnight did it then dissolve in the usual way. The material, subsequently well washed and dried, was extracted with ether, and the fluorescent extract was evaporated to dryness and the residue washed first with benzene and then with water to remove acid. It was again extracted with ether, benzene added to the extract, and the red flocks which separated on evaporation were washed with benzene. The small amount of bright red powder thus isolated had the properties of deoxysantalin, and has hitherto failed to yield crystals. A methoxy-determination gave CH_3 = 6·58 per cent. It thus seems that the dyeing property of sanderswood is due rather to the deoxysantalin than to santalin itself, and again, although sanderswood is specially rich in colouring matter, it is astonishing how little of this comes into play in the dyeing process.

Some proof of this was obtained by dyeing wool with 60 per cent.

of sanderswood, and at the end of the operation employing the residual wood twice for dyeing fresh material. The first pattern possessed the usual colour, the second was pale pink, and the third was practically undyed, indicating that all the colouring matter soluble in water had then been removed. The woody matter, however, now yielded to boiling alcohol 13·8 per cent. of extract compared with the 19·4 per cent. originally present, and this consisted of a dark red, resinous mass and contained much santalin. Even, therefore, if it be presumed that all the soluble matter removed from the wood in the dye-bath is colouring matter, it is evident that the larger proportion present therein, owing to its insoluble nature, remains undissolved and takes no part in this operation.

Weidel (*loc. cit.*), by removing the colouring matter from sanderswood with dilute alkali hydroxide, precipitating with acid, and extracting the product with ether, isolated two crystalline compounds, namely, santal, $C_8H_6O_3$, and a red substance, $C_{14}H_{12}O_4$, very sparingly soluble in the ordinary solvents. Experiments to isolate these compounds by Weidel's process have hitherto failed, although, as shown later, they can be obtained from barwood. As in any case they are difficult to prepare, especially by his method, a definite statement as to their non-existence in sanderswood cannot at present safely be made.

On the other hand, sanderswood contains, like camwood, a colourless, phenolic substance not removed from ether by means of hydrobromic acid, which does not appear to crystallise readily.

Barwood.

A comparison of the colouring matter of this wood with those of sanderswood and camwood appeared to be interesting, but owing to lack of opportunity its examination in this respect could not be carried out at all completely, and the extract from only 450 grams of the wood has as yet been employed.

The only important work on this subject is that of Anderson (*Journ. Chem. Soc.*, 1876, ii, 582), which, curiously enough, has been ignored in the later literature. He obtained from the wood colourless crystals, which he termed baphiin, and from this product by means of alkali solution prepared baphic acid, soluble in this reagent, and baphinitin and baphinitone, insoluble, all of which were also crystalline. According to Ryan and Fitzgerald (*Proc. Royal Irish Acad.*, 1913, **30**, 106), baphinitone is identical with homopterocarpin, and possesses the formula $C_{17}H_{16}O_4$. Anderson also considered the wood to contain three colouring matters, one

soluble in ether, a second soluble in alcohol and insoluble in ether, and a third which is crystalline.

The alcoholic extract* of barwood was worked up in the same manner as that of camwood and sanderswood, and a colouring matter corresponding with the santalin and *iso*santalin of the latter was isolated. After treatment with pure ethyl acetate, it consisted of a chocolate-red powder indistinguishable in appearance from santalin. The analysis of this substance and of its potassium salt gave the following result:

Found: C = 65·8; H = 4·6; CH_3 = 7·43; K = 3·06.

On heating, it commenced to soften at 240°, apparently decomposing, and at 270° had the appearance of a honeycombed, carbonaceous mass, a behaviour very similar to that given by santalin; its colour reactions, which were violet with alcoholic ferric chloride, crimson with alcoholic hydrobromic acid, and dull red with dilute sodium hydroxide solution, were the same as those given by this colouring matter. It thus appears extremely probable that this is identical with santalin.

The ethereal liquid obtained during the isolation of this substance, which corresponded with that termed *B* in connexion with camwood, was evaporated to dryness, the residue again dissolved in a little alcohol, and poured into ether. The solution decanted from a trace of resinous precipitate was washed once with water and treated drop by drop with fuming hydrobromic acid until all the colouring matter had been removed from the ether as hydrobromide (*C*). After washing with water, the ether, on evaporation to dryness, gave an almost colourless, crystalline residue. This was digested with benzene to remove a trace of a substance resembling pterocarpin,† dissolved in hot alcohol, and the solution diluted with a little water. The large leaflets which separated on cooling and became opaque on drying, owing to loss of water of crystallisation, were recrystallised from absolute alcohol. The yield was 0·7 gram.

Found: C = 63·95; H = 4·20; CH_3 = 5·04.

$C_{16}H_{12}O_6$ requires C = 64·0; H = 4·0; CH_3 = 5·0 per cent.

This compound appears to be the santal described by Weidel (*loc. cit.*) as existing in sanderswood; he assigned to it the formula $C_8H_6O_3,\frac{1}{2}H_2O$, and obtained from it a dibromo-compound,

* The residue obtained by evaporating the alcoholic extract to dryness on solution in 75 per cent. alcohol gives gradually a considerable deposit of this product.

† The complete removal of this substance from the colouring matter by either the lead acetate or baryta method of precipitation is difficult to effect.

$C_8H_4O_3Br_2$. Weidel, however, did not ascertain the presence of a methoxy-group, and its analysis in this respect indicates that it possesses the formula $C_{15}H_9O_5(O{\cdot}CH_3)$. Santal melts at 222—223°, is readily soluble in dilute alkali hydroxide, and sparingly so in absolute alcohol, from which it crystallises in thin plates or flat needles. With alcoholic lead acetate, it gives a colourless precipitate, and with alcoholic ferric chloride a violet-black coloration, although this, according to Weidel, is dark red. On acetylation, it gives a well-defined, crystalline acetyl derivative, and seems to be very similar to Anderson's baphic acid (*loc. cit.*). The hydriodic acid liquid from the Zeisel determination contained crystals, and these, after removal of the acid, separated from dilute alcohol in small, colourless, flat needles melting at 270—273°, apparently with decomposition. This new compound, for which the name *santol* is proposed, would appear to possess the formula $C_{15}H_{10}O_6$, and this it is hoped to confirm at a later period. Its solution in dilute alkali hydroxide, at first almost colourless, rapidly develops a reddish-violet tint, and the liquid on acidification deposits yellow crystals. If the acid mixture is boiled, these become colourless, apparently with regeneration of santol, for when collected and washed, the product can again be made to produce the same changes. Santol thus appears to contain a lactone group. With lead acetate, it gives a colourless precipitate, and with alcoholic ferric chloride a brownish-black coloration.

The hydrobromic acid liquid (*C*) obtained during the isolation of santal, decanted from any insoluble matter, was diluted with water, the precipitate repeatedly treated with water to decompose the hydrobromide, and the product, when dry, dissolved in a little ethyl acetate, the solution being allowed to evaporate spontaneously. After several days, minute specks were present in the viscous fluid, and this was now stirred with a mixture of pure ether and ethyl acetate, the insoluble product being collected and washed with ethyl acetate In order to remove santal, which was found to be present, it was digested at the boiling point for one hour with absolute alcohol, and the glistening mass of bright red crystals (0·4 gram) analysed. (Found: C = 67·3; H = 4·8; CH_3 = 9·77.)

This had the reactions of the compound $C_{14}H_{12}O_4$ (C = 68·8; H = 4·9) described by Weidel as existing in sanderswood, but probably contained still a little santal, and this seemed certain by a crystallisation of the substance from alcohol, when the 0·0756 gram thus obtained gave the higher figures, C = 67·86; H = 4·84 per cent. A further purification has not been possible, but there can be little doubt that this compound still retained santal, and that when completely freed from this, Weidel's formula, $C_{14}H_{12}O_4$, represents its

composition. On the other hand, the result of the Zeisel determination indicates that Weidel's formula can scarcely be correct, and that the true formula, based on his figures, would appear to be $C_{22}H_{13}O_4(O\cdot CH_3)_3$ or $C_{22}H_{15}O_4(O\cdot CH_3)_3$, the former of which requires C = 69·1; H = 5·06; CH_3 = 10·3 per cent. In case this is correct, this compound, for which the name *santalone* is proposed, has the composition of *deoxysantalin monomethyl ether*, and, indeed, its general properties are in harmony with this suggestion.

Santalone is sparingly soluble in most solvents, and crystallises from alcohol in small, glistening red leaflets. It readily dissolves in alcoholic hydrobromic acid with a bright scarlet, in dilute alkalis with a fairly permanent red, whereas alcoholic ferric chloride produces a violet colour. Alcoholic potassium acetate does not appear to cause the separation of a potassium salt. When heated, the purest preparation obtained up to the present darkened about 280° and melted at 300°.

The hydriodic acid liquid from the Zeisel determination contained a blackish-green, metallic-looking resin, which was soluble in alkali hydroxide with a violet colour, rapidly becoming brown in the air and closely resembling the product given in the same way by deoxysantalin.

Several years ago Herz and Perkin (Thorpe's "Dictionary of Applied Chemistry," 1913, Vol. IV., 629) isolated both these compounds from barwood by Weidel's method in very small amount, but in order to obtain any quantity of this rare material, the process of extracting large quantities of resinous colouring matter with ether for several days proved impracticable. On the other hand, the operation was not always successful, and this appeared to depend on the alteration of the main bulk of the constituents of the wood soluble in ether, other than santal and santalone, during the alkaline extraction into resinous products insoluble in this medium.

The mother liquors from which the santalone had been isolated contained a considerable amount of insoluble colouring matter resembling deoxysantalin, which, however, was not closely examined.

Summary of Results.

The results of this investigation indicate that the more insoluble colouring matter of camwood, here termed iso*santalin*, is most simply expressed as $C_{22}H_{18}O_6(OMe)_2$. It is isomeric with the santalin of sanderswood, and for this the same formula is therefore proposed in place of $C_{14}H_{11}O_4(OMe)$ suggested by Cain and

Simonsen. Although santalin from sanderswood appears to be identical with the colouring matter which can be similarly isolated from barwood, the *iso*santalin of camwood differs from both these in that it possesses not only a much higher decomposition point, but gives distinctly bluer shades on mordanted woollen cloth. *iso*Santalin and santalin are respectively accompanied in the dyewood by the more readily soluble colouring matters *deoxyisosantalin* and *deoxysantalin*, which again are isomeric, and for which the formula $C_{22}H_{16}O_5(OMe)_2$ or $C_{22}H_{18}O_5(OMe)_2$ is proposed. The connexion between the santalins and deoxysantalins is at present uncertain, and the acetyl determinations do not favour the view which at first suggested itself, that the former differ from the latter in possessing an additional hydroxyl group. There is some probability that the deoxy-compounds are converted by oxidation in alkaline solution into the santalins, but experiments on this point and on their behaviour towards *p*-benzoquinone in alcoholic solution have for the present been laid aside. None of these compounds has as yet been obtained in a definitely crystalline condition, and the opinion is expressed, at least as regards santalin, that if this is to be effected some special process, perhaps of the character by which crystalline hæmatein is prepared from logwood, will have to be devised. Meier's santalin (*loc. cit.*), which it is suggested is rather deoxysantalin than Cain and Simonsen's santalin, was described by this author as crystalline, and it is quite possible that both deoxy- and deoxy*iso*-santalin, here obtained, contain still some impurity which renders crystallisation more difficult. The potassium salts of *iso*santalin and santalin possess the formula $C_{72}H_{65}O_{24}K$ or $C_{96}H_{87}O_{32}K$, and this fact, coupled with the exceedingly small depression of the freezing point given by their acetyl compounds in naphthalene, indicates that either these colouring matters possess a very high molecular weight or that this depression is abnormal. The effect of other solvents remains to be investigated, but as Cain and Simonsen, employing phenol, obtained with santalin a molecular weight of 257, the latter suggestion would appear to be correct.

Santal and Weidel's substance, $C_{14}H_{12}O_4$ (?), now termed *santalone*, have been found to exist in barwood, and the formulæ considered applicable to these compounds are respectively $C_{15}H_9O_5(OMe)$ and $C_{22}H_{15}O_4(OMe)_3$, the latter being possibly a *deoxysantalin monomethyl ether*. These compounds will be further examined when opportunity arises, and it is possible that by their study some clue to the constitution of both santalin and *iso*santalin will result.

Note on St. John's Wort.

According to Keegan (*Chem. News*, 1915, **111**, 290), St. John's wort, *Hypericum perforatum*, contains much flavone, which seemed to be similar to gossypetin. Desiring a further supply of this colouring matter, previously only known to be present in quantity in cotton flowers, the yellow colouring matter of St. John's wort was submitted to examination. A concentrated alcoholic extract of the dried material was poured into water, the mixture shaken with ether to remove wax, etc., and the clear liquid digested at the boiling point with a little sulphuric acid. When cold, the precipitate was collected, and in this condition dissolved in alkali with a green shade somewhat similar to that given by gossypetin. After removal of impurity by solution in ether, the yellow product was crystallised from dilute alcohol, and on treatment with alkali hydroxide now gave a pure yellow tint. The acetyl compound melted at 194—196°, and when mixed with acetyl quercetin did not depress the melting point of the latter. The benzoyl compound melted at 185—186°, and this was identical with that of pentabenzoyl quercetin obtained by means of benzoic anhydride. The colouring matter of St. John's wort consists, therefore, of quercetin, and no gossypetin is present.

CLOTHWORKERS' RESEARCH LABORATORY,
DYEING DEPARTMENT,
THE UNIVERSITY, LEEDS. [*Received, January 3rd*, 1918.]

XVII.—*Studies on the Walden Inversion. Part VI. The Influence of the Solvent on the Sign of the Product in the Conversion of Phenylbromoacetic Acid to Phenylaminoacetic Acid.*

By GEORGE SENTER and STANLEY HORWOOD TUCKER.

IN previous papers (Senter and Drew, T., 1915, **107**, 638; 1916, **109**, 1091) it was shown that when the halogen atom in optically active phenylchloroacetic acid is displaced by the amino-group by the direct action of ammonia, the sign of the amino-acid depends on the nature of the solvent in which the reaction occurs. In water, the higher aliphatic alcohols, and benzonitrile, the resulting amino-acid has the opposite sign to the chloro-acid taken, whereas

in liquid ammonia, acetonitrile, and the lower aliphatic alcohols, the amino-acid has the same sign as the original chloro-acid. In all cases, the amino-acids obtained were considerably less active than the optically pure acids, so that considerable racemisation occurred during the displacement. In order to throw further light on this question, a similar investigation has now been carried out with phenylbromoacetic acid, and the results are described in the present paper. In addition to the amino-acid, iminodiphenyldiacetic acid is also formed in all the solvents used. The reactions are as follows:

$$Br\cdot CHPh\cdot CO_2\cdot NH_4 + NH_3 \longrightarrow NH_2\cdot CHPh\cdot CO_2H + NH_4Br,$$

$$2Br\cdot CHPh\cdot CO_2\cdot NH_4 + NH_3 \longrightarrow CO_2H\cdot CHPh\cdot NH\cdot CHPh\cdot CO_2H + 2NH_4Br.$$

The method of experiment was similar to that used in the case of the chloro-acid (*loc. cit.*). In all cases, *l*-phenylbromoacetic acid was used, and the reactions took place at the ordinary temperature. As the amino-acid and imino-acid from most of the solvents were opposite in sign, special care was taken to ensure the purity of the products before their optical activity was determined. The rotatory power of the products was measured with mercury green light ($\lambda = 5461$), in most cases also with sodium light, and in some cases with the mercury violet ($\lambda = 4359$). In numerous measurements with amino-acids of different degrees of activity, it has been found that the ratio $[\alpha]_D : [\alpha]_{5461}$ is 0·84. The observations, both with the amino-acid and imino-acid, were made in *N*-hydrochloric acid solution.

The main results are given in the accompanying table.

TABLE I.

Action of Ammonia on l-Phenylbromoacetic Acid.

Solvent.	Value of $[\alpha]_{5461}$ for amino-acid formed.	Value of $[\alpha]_{5461}$ for imino-acid formed.
Liquid NH_3	− 38°	+ 161°
Water	+ 89	+ 177
$CH_3\cdot OH$	+ 2	+ 180
$C_2H_5\cdot OH$	+ 2	+ 120·5
$C_3H_7\cdot OH$ (*n*)	+ 5·5	+ 187·5
$C_3H_7\cdot OH$ (*iso*)	+ 3·2	+ 173·5
$C_4H_9\cdot OH$ (*n*)	+ 17·7	+ 206
$(CH_3)_3C\cdot OH$	+ 22	+ 193
$C_5H_{11}\cdot OH$ (*n*)	+ 130	+ 170
$CH_3\cdot CN$	− 48·3	[+ 66·7]

The value of $[\alpha]_D^{20}$ for optically pure phenylaminoacetic acid is $\pm 157{\cdot}8°$ (Fischer and Weichhold, *Ber.*, 1908, **41**, 1285), corresponding with $[\alpha]_{5461}^{20}$ $\pm 187{\cdot}8°$.

The amino-acid from each experiment was separated in two crops (p. 146), which were examined separately as regards activity. The second much smaller crop was in almost all cases the more active, corresponding with the fact that the active acids are considerably more readily soluble in water than the racemic. The numbers in the second column represent the mean activity of the whole crop of amino-acid in each case, and as the latter could be isolated fairly completely from the products of reaction, they also represent with considerable accuracy the relative activities of the acids formed in the different solvents. The yields of imino-acid were in all cases smaller than those of the amino-acid, but relatively greater than those obtained in the corresponding experiments with the chloro-acid.

The table shows that in all the solvents except water and acetonitrile, the sign of the amino-acid formed is opposite to that of the amino-acid taken. Further, considerable racemisation occurs in all the solvents used, more particularly in the lower alcohols. The imino-acid formed has in every case the opposite sign to that of the original bromo-acid.

As interesting results were obtained as to the effect of ammonium chloride on the reaction with phenylchloroacetic acid, the effect of ammonium bromide on the reaction now under consideration was examined. In aqueous ammonia, the amino-acid from the solution containing no ammonium bromide gave $[\alpha]_{5461} + 131°$, whilst in an exactly corresponding experiment, except that the mixture contained 2 grams of ammonium bromide in 10 c.c., the value $[\alpha]_{5461} + 122°$ was obtained for the amino-acid. This slight difference is readily accounted for by the greater amount of washing necessary in the latter case to free the amino-acid from ammonium bromide. In exactly comparable experiments in liquid ammonia, the amino-acid from the solution containing no ammonium bromide gave $[\alpha]_{5461} - 38°$; that from the solution containing the salt was quite inactive. As ammonium bromide is one of the products of reaction, it doubtless causes some racemisation in certain solvents to which it is not originally added. In the higher alcohols and acetonitrile, it separates in the solid form as the reaction proceeds, and therefore cannot appreciably influence the activity of the amino-acid formed.

Discussion of Results.

Although in many respects the results obtained with phenylbromoacetic acid correspond with those found for the chloro-acid (*loc. cit.*), there are also important differences which will undoubtedly prove of great importance in elucidating the mechanism of the reactions. The chief resemblances are that in both cases the amino-acids obtained from water and the higher alcohols as solvents are opposite in sign; those from liquid ammonia and acetonitrile similar in sign to the original phenylhalogen acid. Further, the effect of ammonium chloride and bromide respectively on the reactions in aqueous and in liquid ammonia is similar in the two cases. The main difference is that with the lower aliphatic alcohols the amino-acid from phenylbromoacetic acid is opposite in sign, from phenylchloroacetic acid similar in sign, to the original phenylhalogen acid. The quantitative results are shown in the accompanying table.

TABLE II.

Solvent (alcohol)	Methyl.	Ethyl.	Propyl.	*iso*Propyl.
Amino-acid from *l*-bromo-acid	+ 2°	+ 2°	+ 5·5°	+ 3·2°
Amino-acid from *d*-chloro-acid	+ 7·5	+ 34	+ 10	+ 5

In a further experiment with *l*-phenylchloroacetic acid in ethyl alcohol, the average activity of the resulting amino-acid was $[\alpha]_{5461}$ −51°, which fully confirms the earlier results of Senter and Drew (*loc cit.*). The slightly higher activity in the former case is doubtless due to the lower temperature at which the reaction took place. It may be added that not much confidence from a quantitative point of view can be placed in the results with phenylchloroacetic acid in methyl alcohol, as owing to the simultaneous formation of phenylmethoxyacetic acid only 0·1 gram of phenylaminoacetic acid was obtained, and its activity was doubtless considerably reduced during washing with water. With the other alcohols, good yields of amino-acid were obtained.

The results are probably to be accounted for on the basis of the theory put forward in the succeeding paper (Senter, Drew, and Martin, *loc. cit.*, p. 151), that the action of ammonia on halogen-substituted acids proceeds by two simultaneous reactions, resulting in the formation of *d*- and *l*-amino-acids respectively, and that the relative proportion of the amino-acids formed depends on the nature of the halogeno-acid, of the solvent, and of other factors. In the lower alcohols, the reaction leading to the formation of an amino-acid of the same sign as that of the halogeno-acid predominates

slightly in the case of the chloro-acid, whilst the other reaction predominates slightly in the case of the bromo-acid. In liquid ammonia, the relative rates of the two reactions are influenced considerably by the presence of ammonium bromide. So far, it is not possible to state with certainty which of these reactions is normal and which abnormal, but it is hoped that kinetic investigations will throw light on these and other points.

From the data in table I, it is evident that the amino-acid from the lower alcohols is much more racemised than that from the higher alcohols. This effect, however, is not determined solely by the molecular weight of the alcohol, as the products from isomeric alcohols (the two propyl alcohols, also *n*-butyl alcohol and trimethylcarbinol) are not of the same activity.

Iminodiphenyldiacetic Acid.—The isolation of this acid from the products of reaction is described in the experimental part, and it is there shown that the activity of the optically pure acid probably does not much exceed ±210°. As the table shows, the products from all the solvents are very active; with the doubtful exception of the acid from acetonitrile, $[\alpha]_{5461}$ exceeds 120°. The imino-acids obtained by the action of ammonia on the *d*-chloro-acid (Senter and Drew, *loc. cit.*) were also very active; in aqueous ammonia and ammonium chloride, *n*-butyl alcohol and *n*-heptyl alcohol, the respective values for $[\alpha]_{5461}$ were 188°, 167°, and 162° approximately.

It is shown in the succeeding paper that a corresponding imino-acid, namely, α-imino-ββ-diphenyldipropionic acid, is obtained by the action of ammonia on α-bromo-β-phenylpropionic acid in all the solvents examined; in this case, however, the imino-acid has the same sign as the original bromo-acid.

It has already been pointed out (Senter and Drew, *loc. cit.*, p. 1097) that imino-acids of this type might be formed by the reaction of one molecule of ammonia with two molecules of halogeno-acid (p. 141), or by the interaction of one molecule of halogeno-acid and one molecule of amino-acid:

$$Br{\cdot}CHPh{\cdot}CO_2H + NH_2{\cdot}CHPh{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CHPh{\cdot}NH{\cdot}CHPh{\cdot}CO_2H.$$

On the former assumption, the fact that a highly active imino-acid of the same sign is obtained from the same halogeno-acid in all solvents is readily accounted for. The latter view of the mechanism of the reaction would apparently imply that the *l*-bromo-acid reacts with one of the optically active forms of the amino-acid much more rapidly than the other. Thus, it can be calculated from the data in table I that the amino-acid from heptyl alcohol contains

about 85 per cent. of the *d*- and 15 per cent. of the *l*-form, that from liquid ammonia 40 per cent. of the *d*- and 60 per cent. of the *l*-form, whereas from both solvents *d*-imino-acids of high and practically equal activity are obtained. It is well known that an optically active compound may react with one stereoisomeride more rapidly than with the other (compare Marckwald and Meth, *Ber.*, 1905, **38**, 801; Marckwald and McKenzie, *Ber.*, 1899, **32**, 2130), but the differences are usually small, and the predominance of one reaction, which the explanation now under consideration would imply, is so great as to be highly improbable. This question cannot easily be examined experimentally on account of the difficulty of finding a suitable solvent for the amino-acid, but the following observation lends some support to the view that the amino-acid is not an intermediate compound in the formation of the imino-acid. *r*-Phenylaminoacetic acid and *l*-phenylchloroacetic acid, along with triethylamine (which dissolves the former acid only to a small extent), were kept at the ordinary temperature for one hundred and five days. No imino-acid could be isolated from the products, and apparently no reaction had taken place. The conclusion that the imino-acid is formed by the interaction of two molecules of bromo-acid and ammonia therefore appears most in harmony with the experimental results.

It remains to account for the fact that whereas *l*-phenylbromo-acetic acid yields a *d*-imino-acid, *l*-benzylbromoacetic acid yields an *l*-imino-acid. As the two *l*-bromo-acids are probably of the same configuration, this result implies either that the two *l*-imino-acids differ in configuration or that a Walden inversion occurs in the formation of one of the imino-acids. Although the latter explanation is the more probable, the former cannot be ruled out, since both for amino-acids and imino-acids the magnitude and even the sign of the rotation are doubtless complicated by internal salt-formation, hydration, and other factors. The effect of change of temperature and addition of electrolytes on the optical activity of the two imino-acids would throw light on the question of their relative configuration (compare Clough, T., 1915, **107**, 1517).

Experimental.

r-Phenylbromoacetic acid was resolved with morphine according to McKenzie and Walker's method (T., 1915, **107**, 1685). The pure *l*-acid melted at 87—88° and gave $[\alpha]^{20}_{5461}$ −178·5°, in excellent agreement with the results of these authors. The method of experiment was similar to that used in the case of the chloro-acid, except that the time of reaction was considerably shorter, in accord-

ance with the greater reactivity of the bromo-acid (Senter and Tucker, T., 1916, **109**, 690).

The method of isolating the products already given (Senter and Drew, *loc. cit.*, p. 1098) requires amplification in view of the fact that the separation of the imino-acid was not described. The earlier account is applicable up to the stage at which the first crop of amino-acid has been isolated, and the acidified solution, containing any remaining amino-acid and the other products of reaction, has been extracted several times with ether to remove any unchanged bromo-acid and any non-basic acids (hydroxy-acid, alkyloxy-acid) formed during the reaction. To the aqueous acid solution, which contains the imino-acid and any remaining amino-acid as hydrochlorides, the washings of the first crop of amino-acid are added, the whole is evaporated to dryness to remove excess of hydrochloric acid, the residue dissolved in aqueous ammonia, and the solution evaporated to the stage at which the stirred mass becomes pasty and remains faintly alkaline. In this way, by decomposition of its ammonium salt, the amino-acid is separated in the solid form, and the soluble ammonium salt of the imino-acid remains undecomposed. To the alkaline product cold water is added and the mixture filtered; the residue, after washing with cold water, constitutes the second crop of amino-acid. To the filtrate hydrochloric acid is added until the solution is acid to Congo-red; on keeping, the imino-acid separates in clusters of long needles. If the solution is kept faintly acid, the imino-acid can be separated practically completely; the final solution has a slight activity of the same sign as the amino-acid, due to a trace of the latter which is present on account of its sparing solubility in water.

As already indicated, the method of separating the amino-acid and imino-acid depends on the fact that the unstable ammonium salt of the former is decomposed on heating in solution, the amino-acid separating, whilst the ammonium salt of the imino-acid is stable when heated, even in neutral solution, but decomposes when heated in the dry state at 100°. That the separation was effective was proved in various ways, most convincingly by an experiment in which some imino-acid was added to 0·2 gram of the *r*-amino-acid and the separation carried out in the usual way. The amino-acid obtained proved to be quite inactive, whilst the imino-acid showed its full activity.

The purity of the amino-acid was checked in all cases by a determination of its equivalent by conversion of a known weight into the hydrochloride, and also in some cases by determination of the nitrogen by the absolute method. As in all cases results practic-

ally identical with the calculated values were obtained, it appears unnecessary to quote them in detail.

The activity both of the amino- and imino-acids was measured in 0·984*N*-hydrochloric acid in a 2-dcm. tube at the ordinary temperature. For the first crops of amino-acid, the solutions contained 1 gram in 100 c.c. of solution ($c=1·0$), whilst usually the whole of the small second crop was used in making up 10 c.c. of solution for activity measurements.

In order to obtain approximately pure *d*-imino-acid, the products from several experiments were recrystallised from *N*-hydrochloric acid. In one experiment, the third recrystallisation raised the rotation from $[\alpha]_{5461}$ 196° to 200°; in a second experiment, the final crop gave $[\alpha]_{5461}$ +209°. The process could not be carried further owing to want of material, but it is probable that the value of $[\alpha]_{5461}$ for the optically pure acid does not much exceed 210°.

Water.

A solution of 0·5 gram of the *l*-bromo-acid in 10 c.c. of aqueous ammonia (35 per cent. NH_3) was kept at 18° for eight days. The first crop of amino-acid (0·16 gram) had α_{5461} +1·78°, $[\alpha]_{5461}$ +89°; the second crop was so small that the activity could not be measured. The imino-acid (0·015 gram), $c = 0·113$, had α_{5461} + 0·40, $[\alpha]_{5461}$ +177°.

In two parallel experiments to determine the effect of ammonium bromide on the reaction, solutions of 0·5 gram of the *l*-bromo-acid in 10 c.c. of aqueous ammonia (35 per cent. NH_3), and in one case 2 grams of ammonium bromide, were kept for nine days at 10°. The solutions remained clear throughout. From the solution containing ammonium bromide, the amino-acid (0·17 gram) gave α_{5461} +2·44°, $[\alpha]_{5461}$ +122°; that from the other solution (0·14 gram) gave α_{5461} 2·62°, $[\alpha]_{5461}$ +131°.

Liquid Ammonia.

A solution of 0·5 gram of the *l*-bromo-acid in 10 c.c. of liquid ammonia, kept in a sealed tube at 15° for eight days, gave as first crop 0·20 gram of amino-acid, α_{5461} −0·76°, $[\alpha]_{5461}$ −38°, and a very small second crop. The imino-acid (0·03 gram), $c=0·28$, had α_{5461} +0·90, $[\alpha]_{5461}$ +161°. In an exactly corresponding experiment, except that the solution contained also 2 grams of ammonium bromide and was kept for thirteen days, the first crop of amino-acid (0·264 gram) and also the small second crop were inactive. The

imino-acid (0·0086 gram) gave for $c=0·086$ $\alpha_{5461}+0·34°$, $[\alpha]_{5461}+198°$. As, owing to the large amount of ammonium bromide in the second experiment, repeated washing of the first crop of amino-acid was necessary for purification, it cannot be affirmed that racemisation was quite complete, but in any case the activity of the amino-acid formed in these circumstances must be extremely small.

Methyl Alcohol.

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of methyl alcohol saturated with dry ammonia, kept for fifteen days at 15°, gave a first crop of amino-acid (0·12 gram) with $\alpha_{5461}+0·04°$, $[\alpha]_{5461}+2°$, and a second crop (0·013 gram) which was quite inactive. The imino-acid (0·0025 gram) gave for $c=0·025$ $\alpha^{15}_{5461}+0·09°$, $[\alpha]^{15}_{5461}+180°$.

In an exactly corresponding experiment, except that the solvent was partly saturated with ammonia (3 c.c. of the solvent saturated with ammonia were added to 12 c.c. free from ammonia) and the solution kept for eighteen days at 15°; the first crop of amino-acid (0·077 gram) was inactive, the second crop (0·027 gram) gave for $c=0·265$ $\alpha_{5461}+0·06$, $[\alpha]_{5461}+11°$. The imino-acid (0·025 gram) gave for $c=0·245$ $\alpha_{5461}+0·94°$, $[\alpha]_{5461}+192°$.

The small yields of amino-acid are due to the simultaneous formation of phenylmethoxyacetic acid and (in the second experiment) to the fact that the reaction was incomplete.

Ethyl Alcohol.

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of the solvent saturated with dry ammonia, kept for fifteen days at 15°, gave a first crop of amino-acid (0·275 gram) having $\alpha_{5461}+0·04°$, $[\alpha]_{5461}+2°$, and a second crop (0·02 gram) which was inactive. The imino-acid (0·081 gram) gave for $c=0·224$ $\alpha^{18}_{5461}+0·54°$, $[\alpha]^{18}_{5461}+120·5°$.

In a second exactly corresponding experiment, except that the solution was kept at 0° for ten days and at 20° for two days, the first crop of amino-acid (0·30 gram) gave $\alpha_{5461}+0·06°$, $[\alpha]_{5461}+3°$; the second crop (0·012 gram) gave no measurable rotation. The imino-acid (0·028 gram), $c=0·155$, gave $\alpha_{5461}+0·34°$, $[\alpha]_{5461}+109°$.

The filtrate, after separation of the imino-acid, in the first experiment had a slight negative rotation, and in the second experiment was inactive, whereas in all other solvents the final filtrate had a slight activity corresponding in sign with the amino-acid. No satisfactory explanation of this result has been found. It is possible

that in ethyl alcohol traces of a lævorotatory compound are formed in such amount as to compensate, or in some cases over-compensate, the slight activity due to the amino-acid always present in traces in the final filtrate.

n-*Propyl Alcohol.*

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of the solvent, saturated with ammonia at 0° and kept at 15° for fifteen days, gave a first crop of amino-acid (0·24 gram) of α_{5461} +0·09, $[\alpha]_{5461}$ +4·6°, and a second crop (0·007 gram), which for $c=0·07$ gave α_{5461} +0·05°, $[\alpha]_{5461}$ +35·7°. The imino-acid (0·087 gram) gave for $c=0·2$ α_{5461} +0·75°, $[\alpha]_{5461}$ +187·5°.

iso*Propyl Alcohol.*

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of the solvent saturated with ammonia and kept for sixteen days at 15° gave a first crop of amino-acid (0·29 gram) of α_{5461} +0·05°, $[\alpha]_{5461}$ +2·5°, and a second crop, which for $c=0·127$ gave α_{5461} +0·05°, $[\alpha]_{5461}$ +19·7°. The imino-acid (0·081 gram) gave for $c=0·17$ α_{5461} +0·59°, $[\alpha]_{5461}$ +173·5°.

n-*Butyl Alcohol.*

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of the solvent (b. p. 117°), saturated with ammonia and kept for twelve days at 15°, gave a first crop of amino-acid (0·22 gram) of α^{18}_{5461} +0·25°, $[\alpha]^{18}_{5461}$ +12·5°, and a second crop (0·009 gram) gave for $c=0·09$ α_{5461} +0·18°, $[\alpha]_{5461}$ +147°. The imino-acid (0·1 gram, m. p. 208° decomp.) gave for $c=0·17$ α^{17}_{5461} +0·70°, $[\alpha]^{17}_{5461}$ +206°. The readings for the first and third crops were repeated after a lapse of three months; the values found were +0·24° and +0·68° respectively, so that the activity of both acids remains practically unaltered by keeping in *N*-hydrochloric acid solution.

Trimethylcarbinol.

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of the solvent saturated with ammonia at 0° and kept for twenty-five days at 15° gave a first crop of amino-acid (0·17 gram) of α_{5461} +0·08°, $[\alpha]_{5461}$ +4°, and a second crop (0·0275 gram), which for $c=0·275$ gave α^{16}_{5461} +0·74°, $[\alpha]^{16}_{5461}$ +134·5°. The imino-acid (0·12 gram—the largest proportion in any solvent) gave for $c=0·15$ α_{5461} +0·58°, $[\alpha]_{5461}$ +193°.

n-Heptyl Alcohol.

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of solvent (b. p. 174—176°) saturated at 0° with ammonia and kept for sixty-two days at 15° gave a first crop of amino-acid (0·12 gram) of α_{5461} +2·51°, $[\alpha]_{5461}$ +125·5°, and a second crop (0·0173 gram), which for c=0·173 gave α_{5461} +0·55°, $[\alpha]_{5461}$ +159°. The imino-acid (0·058 gram) gave for c=0·165 α_{5461} +0·56°, $[\alpha]_{5461}$ +170°.

Acetonitrile.

0·75 Gram of the *l*-bromo-acid was dissolved in 15 c.c. of the solvent and ammonia passed in at 0°. A white, flocculent precipitate appeared almost immediately, and when the solution was saturated, the tube contained a voluminous, white paste which, on keeping in the ice-chest overnight, set to a jelly. It was kept at 55° for a few days, but on showing no change it was kept at the ordinary temperature for a further ninety days. Gradually the jelly gave place to a white, flocculent precipitate contained in a mobile liquid (compare Senter and Drew, *loc. cit.*, p. 1101). The first crop of amino-acid (0·375 gram), separated from this precipitate in the ordinary way, gave α_{5461} −0·71°, $[\alpha]_{5461}$ −35·5°. The second crop (0·044 gram) gave for c=0·432 α_{5461} −1·37°, $[\alpha]_{5461}$ −158·5°. The imino-acid (0·012 gram), which separated in small, cubical crystals, unlike the clusters of needles obtained from all other solvents, gave for c=0·12 α_{5461} +0·16°, $[\alpha]_{5461}$ +66·7°, and was probably contaminated with some *l*-phenylaminoacetic acid.

Summary.

(1) The amino-acid obtained by the action of ammonia on optically active phenylbromoacetic acid in different solvents is opposite in sign to the bromo-acid when water and certain alcohols are used, but similar in sign to the bromo-acid when liquid ammonia and acetonitrile are employed as solvents.

(2) The amino-acid from the lower aliphatic alcohols as solvents is more racemised than that from the higher alcohols.

(3) The presence of ammonium bromide has little effect on the activity of the amino-acid from aqueous ammonia; it has a great racemising effect when the reaction is carried out in liquid ammonia.

(4) Iminodiphenyldiacetic acid is formed in small quantity in all the solvents used; in all cases it is highly active and of opposite sign to the original bromo-acid.

(5) The mechanism of the formation of the imino-acid is discussed.

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CHEMISTRY DEPARTMENT,
BIRKBECK COLLEGE,
LONDON, E.C.

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XVIII.—*Studies on the Walden Inversion. Part VII. The Influence of the Solvent on the Sign of the Product in the Conversion of α-Bromo-β-phenylpropionic Acid to α-Amino-β-phenylpropionic Acid (Phenylalanine). Iminodiphenyldipropionic Acid.*

By GEORGE SENTER, HARRY DUGALD KEITH DREW, and GERALD HARGRAVE MARTIN.

IN previous papers (Senter and Drew, T., 1915, **107**, 638; 1916, **109**, 1091; Senter and Tucker, this vol., 140) it has been shown that when the halogen atom in phenylchloro- and phenylbromo-acetic acid is displaced by the amino-group by the direct action of ammonia, the optical sign of the resulting amino-acid depends on the nature of the solvent in which the reaction occurs. In the case of the bromo-acid (Senter and Tucker, *loc. cit.*), the amino-acid obtained from liquid ammonia and from acetonitrile has the same sign as the bromo-acid taken, whereas from the other solvents an amino-acid of the opposite sign to the original bromo-acid is produced.

In both the acids referred to the phenyl group is directly attached to the asymmetric carbon atom, and in order to find how the results would be affected by a phenyl group further from the point at which substitution occurs, a similar investigation has now been carried out with α-bromo-β-phenylpropionic acid (benzylbromoacetic acid), $C_6H_5 \cdot CH_2 \cdot CHBr \cdot CO_2H$, and the results are described in the present paper.

The acid was resolved by a slight modification of the method described by Fischer and Carl (*Ber.*, 1906, **39**, 4000); the most

active specimens gave for $[\alpha]_D^{17}$ the value $-10{\cdot}2°$, as compared with $[\alpha]_D^{20}$ $-8{\cdot}3°$, the highest value obtained by Fischer and Carl. Most of the measurements were made with two preparations of the *l*-acid of activity $[\alpha]_D^{17}$ $-8{\cdot}8°$ and $-10{\cdot}2°$ respectively; in a few cases, a dextrorotatory acid of lower activity was used.

The main reaction between ammonia and the ammonium salt of the bromo-acid proceeds according to the equation

$$CH_2Ph{\cdot}CHBr{\cdot}CO_2{\cdot}NH_4 + NH_3 \longrightarrow CH_2Ph{\cdot}CH(NH_2){\cdot}CO_2H + NH_4Br,$$

but in all the solvents a certain proportion of cinnamic acid, $CHPh{:}CH{\cdot}CO_2H$, is formed by elimination of hydrogen bromide. Further, an imino-acid, which is shown to be *α-imino-ββ-diphenyldipropionic acid*, $CH_2Ph{\cdot}CH(CO_2H){\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2Ph$, was isolated from the products of reaction in all the solvents used. This imino-acid, which has not hitherto been described, may be regarded as being formed by the interaction of two molecules of the ammonium salt and one molecule of ammonia, according to the equation

$$2CH_2Ph{\cdot}CHBr{\cdot}CO_2{\cdot}NH_4 + NH_3 \longrightarrow CH_2Ph{\cdot}CH(CO_2H){\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2Ph + 2NH_4Br.$$

The method used in isolating the amino-acid in a pure condition, and the identification and properties of the imino-acid, are fully described in the experimental portion of the paper. The reaction in all cases took place at the ordinary temperature, and as the halogen in this case is much less reactive than in phenylbromoacetic acid (compare Senter and Martin, T., 1917, **111**, 447), the reacting substances were kept in sealed tubes for two or three weeks in the case of liquid and aqueous ammonia and acetonitrile, and for some months in the case of the alcohols, in order to ensure that the changes were practically complete.

The optical activity of the products was determined for the mercury green ($\lambda = 5461$) as well as for sodium light. The measurements with phenylalanine were made in aqueous solution, the concentration in all cases except one (product from benzonitrile, $c = 0{\cdot}646$) being about 1 per cent. ($c = 1{\cdot}0$). The measurements with the imino-acid, on account of its very sparing solubility in water and in dilute hydrochloric acid (p. 162), were made in $1{\cdot}082 \times N/20$-sodium hydroxide. Owing to the small yields of the imino-acid from certain solvents, very dilute solutions had in some cases to be used for the activity measurements, and it was therefore not convenient to make up the solutions to the same concentration, as in the case of the amino-acid. The main results of the investigation are summarised in table I.

TABLE I.

Solvent.	Value of $[\alpha]_D^{17}$ for bromo-acid used.	Value of $[\alpha]_D^{17}$ for phenyl-alanine.	Value of $[\alpha]_{5461}$ for imino-acid
Water (35 per cent. NH_3) ...	− 8·8°	+ 26°	− 34° (c = 0·292)
Water + NH_4Br	− 8·8	+ 27	
Liquid ammonia	−8·8	+10	
,,	−10·2	+7	
Liquid Ammonia + NH_4Br.....	− 8·8 − 10·2	+ 25 + 30	
CH_3·CN	− 8·8	+ 9	
,, ...	+ 5·8	− 8	+ 11 (c = 1·10)
C_6H_5·CN	+ 6·2	− 7	
CH_2·OH	− 8·8	+ 23	− 34 (c = 0·219)
C_2H_5·OH	− 8·8	+ 25	− 35 (c = 0·542)
C_3H_7·OH (n) ...	− 8·8	+ 24	− 34 (c = 0·591)
C_4H_9·OH (n) ...	− 8·8	+ 19	− 33 (c = 0·458)
$(CH_3)_2C$·OH ...	− 8·8	+ 22	− 28 (c = 0·909)
C_6H_5·CH_2·OH ...	+ 6·2	practically inactive.	+ 30 (c = 0·168)

The value $[\alpha]_D^{16}$ for pure *d*-phenylalanine in 2·03 per cent. aqueous solution is + 35·1° (Fischer and Mouneyrat, *Ber.*, 1900, **33**, 2383).

Although, owing to its solubility in water, the amino-acid cannot be isolated quantitatively from the products of reaction, there is no doubt that the numbers given in the table represent fairly accurately the relative activities of the products from the different solvents. As the solubility of the inactive acid is considerably less than that of the active acid (p. 159), a greater proportion of the latter will, as a rule, be removed during the washing of the products with water, and therefore the numbers in the table must be rather lower than those for the amino-acid formed. The yields of phenylalanine from the solutions in benzonitrile and in benzyl alcohol are so small (0·07 and 0·06 gram respectively) that not much confidence can be placed in the results from a quantitative point of view, as the active acid would be largely removed during washing with water.

Fischer and Carl (*loc. cit.*), by the action of aqueous ammonia on a bromo-acid of activity $[\alpha]_D^{20}$ − 8·3, obtained phenylalanine with $[\alpha]_D^{20}$ + 31·78°. The slightly higher value as compared with ours is probably to be accounted for partly by a difference in the amount of washing and partly by the fact that they carried out the early stages of the reaction at a very low temperature.

The formation of an imino-acid in the reaction was overlooked by Fischer and Carl.

Discussion of Results.

The main result of the investigation, so far as the formation of amino-acid is concerned, is that with all the ten solvents used the amino-acid obtained has the same sign, opposite to that of the bromo-acid taken. Further, except in the case of solutions in liquid ammonia, acetonitrile, and benzonitrile, the displacement of bromine by NH_2 takes place without marked racemisation; for reasons already given, the racemisation is even less than appears from the numbers in the table. The effect of ammonium bromide (about 4 grams in 15 c.c.) on the reaction was examined, with remarkable results. Whereas this salt has practically no influence on the activity of the amino-acid obtained from aqueous ammonia, it greatly diminishes the racemisation of the product from liquid ammonia (p. 160).

It is instructive to compare these results with those obtained with phenylbromoacetic acid, as the two acids differ mainly as regards the relative position of the phenyl group with reference to the asymmetric carbon atom (or to the bromine atom). With phenylbromoacetic acid, racemisation was pronounced in all solvents; the amino-acid from liquid ammonia and from acetonitrile had the same sign as the original bromo-acid, whereas in all other solvents it had the opposite sign; finally, whereas ammonium bromide had little effect on the activity of the amino-acid from aqueous ammonia, it produced complete racemisation as regards the amino-acid from liquid ammonia. At first sight there does not seem to be much resemblance in the behaviour of the two acids towards ammonia, but a little consideration puts the matter in a different aspect. The most significant fact appears to be that the phenylalanine from liquid ammonia and from acetonitrile is racemised to a greater extent than that from other solvents, and it is just in those two solvents that the action of ammonia on phenylbromoacetic acid yields an amino-acid opposite in sign to that obtained from all the other solvents. This is most readily accounted for on the assumption that, as compared with other solvents, these two solvents favour the formation of an amino-acid of the same sign as the original bromo-acid, but whereas with *l*-α-bromo-β-phenylpropionic acid the result is the formation of a considerable proportion of both *d*- and *l*-phenylalanine, the product as a whole being dextrorotatory, with *l*-phenylbromoacetic acid the tendency to the formation of the *l*-amino-acid is so much greater that the product as a whole is lævorotatory.

The remarkable effect of ammonium bromide on the two reactions in liquid ammonia can be represented on similar lines; the assump-

tion in this case is that the salt favours the production of an amino-acid having the opposite sign to that of the original bromo-acid. In the case of *l*-α-bromo-β-phenylpropionic acid, the result is a diminution in the racemisation of the resulting *d*-phenylalanine, whilst with *l*-phenylbromoacetic acid, the resulting amino-acid is practically inactive as compared with the formation of a lævorotatory acid in the absence of the salt. It appears justifiable, therefore, to draw the conclusion that the same solvents produce similar effects, of different magnitudes, on the action of ammonia on the active phenylbromoacetic and phenylbromopropionic acids. This conclusion receives strong support from the fact, established in a recent paper (Senter and Martin, T., 1917, **111**, 447), that there is a close analogy in the action of water on the two acids and on their sodium salts.

The same considerations apply to the results with the different alcohols as solvents. The tendency to the formation of an amino-acid of the same sign as that of the original bromo-acid is so much greater in the case of phenylbromoacetic acid that whereas the *d*-phenylalanine from *l*-bromo-β-phenylpropionic acid is scarcely racemised, the amino-acid from *l*-phenylbromoacetic acid, although dextrorotatory, is in most cases only slightly active. In the same circumstances, *l*-phenylchloroacetic acid yields an amino-acid which is slightly lævorotatory.

These results are perhaps best accounted for on the hypothesis that the action of ammonia on the halogen-substituted acids proceeds as two simultaneous reactions, giving rise to *d*- and *l*-amino-acids respectively; for example,

l-phenylbromoacetic acid → *d*-phenylaminoacetic acid
l-phenylbromoacetic acid → *l*-phenylaminoacetic acid,

and that one or the other action predominates, depending on the nature of the halogen acid, the nature of the solvent, and other conditions. The nature of these reactions will be discussed when fuller experimental data are available.

The investigations of Franklin and Kraus (*J. Amer. Chem. Soc.*, 1905, **27**, 191) furnish an interesting analogy to the slight influence of ammonium haloids on the effect of aqueous ammonia as compared with liquid ammonia in the reactions just discussed. Both liquid ammonia and aqueous ammonia react with mercuric chloride as follows:

$$HgCl_2 + 2NH_3 \longrightarrow HgCl_2,2NH_3 \longrightarrow NH_2{\cdot}HgCl + NH_4Cl.$$

In liquid ammonia, the presence of a small quantity of ammonium

chloride prevents the formation of the ammono-basic salt (NH_2·HgCl), whilst in aqueous ammonia a large excess of ammonium chloride is necessary to ensure a pure precipitate of the compound $HgCl_2,2NH_3$.

The above considerations throw some light on the question of the occurrence of racemisation in reactions involving displacement of groups, a subject about which very little is known. This type of racemisation is quite distinct from catalytic racemisation; for example, the conversion of active to inactive mandelic acid by heating with alkali. Catalytic racemisation has in some cases been satisfactorily accounted for on the basis of the formation of intermediate compounds not containing an asymmetric carbon atom (compare Werner, "Stereochemie," p. 52; Lowry, *Rep. Brit. Assoc.*, 1904; McKenzie and Widdows, T., 1915, **107**, 704), and an explanation on similar lines may be found applicable in some cases of displacement racemisation. The results described in this paper, however, make it probable that the racemisation accompanying the displacement of the halogen atom in the phenylhalogenacetic acids is due to the occurrence of two simultaneous reactions, resulting in the formation of *d*- and *l*-amino-acids respectively, and this explanation will probably be found applicable to other examples of displacement racemisation.

With the further data now available, the interconversion of the halogen and amino-derivatives of the two acids in question can be summarised as follows (compare Fischer and Carl, *loc. cit.*; McKenzie and Clough, T., 1909, **95**, 777; Frankland, T., 1913, **103**, 731):

d-Phenylalanine $\xrightarrow{NOBr}$ *d*-α-bromo-β-phenylpropionic acid $\xrightarrow[\text{aqueous } NH_3]{\text{liq. } NH_3}$ *l*-phenylalanine.

d-Phenylglycine $\xrightarrow{NOCl}$ *l*-phenylchloroacetic acid $\xrightarrow[\text{aqueous } NH_3]{\text{liq. } NH_3}$ *l*-phenylglycine. / $\xrightarrow[\text{aqueous } NH_3]{\text{liq. } NH_3}$ *d*-phenylglycine.

These results are very puzzling, and there appears to be little advantage in discussing them more fully until further information as to the mechanism of the reactions involved has been obtained. These investigations are now in progress.

It may be mentioned that Werner, in the course of his investigations on stereoisomeric cobalt compounds (*Annalen*, 1912, **386**, 57), has found that the displacement of a halogen atom in the inner sphere by the NH_3-group takes place more often abnormally than normally (that is, a *cis*-compound is usually obtained from a

trans-, and vice versa), and this is the case both with liquid ammonia and aqueous ammonia as substituting agents.

α-Imino-ββ-diphenyldipropionic Acid.—In the case of the *l*-phenylhalogenoacetic acids (Senter and Drew, *loc. cit.*; Senter and Tucker, *loc. cit.*), it was shown that the action of ammonia in all the solvents examined produced an imino-acid which was dextrorotatory in *N*-hydrochloric acid solution. The imino-acid produced by the action of ammonia on *l*-α-bromo-β-phenylpropionic acid in all the solvents examined is lævorotatory in *N*/20-sodium hydroxide solution. The latter imino-acid is not sufficiently soluble in *N*-hydrochloric acid to be examined in this solvent, but phenyliminoacetic acid was shown to be dextrorotatory in both *N*-hydrochloric acid and *N*/20-sodium hydroxide; thus, a specimen having $[\alpha]^{17}_{5461}$ +190° in *N*-hydrochloric acid ($c=0{\cdot}15$) gave $[\alpha]^{17}_{5461}$ +167° in 1·082*N*/20-sodium hydroxide ($c=0{\cdot}09$). The nature of the solvent is therefore without influence on the sign of the resulting imino-acid in the case of the two acids in question. The theoretical bearing of these results is briefly discussed in the preceding paper (Senter and Tucker, this vol., p. 145).

It is clear from the graphic formula of α-imino-ββ-diphenyldipropionic acid (p. 152) that optical inactivity may be due either to the presence of equal amounts of the *d*- and *l*-acid or to internal compensation. The fact that the melting point of the partly active imino-acid is close to and a few degrees below that of the inactive acid obtained from *r*-α-bromo-β-phenylpropionic acid would accord with the view that the latter acid is the racemic form, but this argument is, of course, not conclusive.

Experimental.

Resolution of r-α-*Bromo-β-phenylpropionic Acid.*

The pure *r*-acid was prepared by Fischer's method (compare Senter and Martin, T., 1917, **111**, 447), and was resolved with brucine by a modification of the method of Fischer and Carl (*loc. cit.*), which consisted in redissolving the precipitated brucine salt at the ordinary temperature in a mixture of alcohol and water (in which it is more readily soluble than in either of the pure solvents) instead of in alcohol at 25° (Fischer and Carl). The details of one experiment are as follows. Thirty grams of the *r*-bromo-acid were dissolved in 150 c.c. of alcohol, and 51·5 grams of anhydrous brucine added, with shaking, at 16°. The solution was filtered, and 900 c.c. of water were added, with stirring. An oil was deposited, which solidified after twenty-four hours. The solid, after being collected

and dried, weighed 53 grams. It was redissolved in a mixture of 250 c.c. of alcohol and 50 c.c. of water, and the solution poured into 1600 c.c. of water. The dried salt finally obtained weighed 26 grams. The acid prepared from it by decomposing with dilute hydrochloric acid and extracting with ether had $\alpha_D^{18} - 13{\cdot}06°$ for $l=1$, corresponding with $[\alpha]_D^{18} - 8{\cdot}80$, and contained the theoretical proportion of bromine. The acid obtained from the first mother liquor was a yellow oil, which gradually deposited a little of the solid *r*-acid. The remainder gave for $\alpha_D^{18} + 8{\cdot}54°$, $l=1$.

In another experiment, in which the brucine salt was three times crystallised, the acid gave $\alpha_{5461}^{17} - 19{\cdot}14°$ and $\alpha_D^{17} - 15{\cdot}22°$ for $l=1$. The density of the liquid was found to be 1·487 at 17° and 1·479 at 25°; hence $[\alpha]_{5461}^{17}$ is $-12{\cdot}9°$ and $[\alpha]_D^{17}$ $-10{\cdot}2°$. In order to obtain a comparison with Fischer's measurements at 20°, the effect of change of temperature on the rotation of another specimen was determined, with the following results: $\alpha_{5461}^{17{\cdot}5} - 16{\cdot}92°$, $\alpha_{5461}^{25} - 17{\cdot}52°$, $\alpha_{5780}^{17{\cdot}8} - 14{\cdot}28°$, $\alpha_{5780}^{25} - 14{\cdot}86°$ for $l=1$. The rotation of α-bromo-β-phenylpropionic acid therefore increases markedly with rise of temperature. The value of $[\alpha]_D$ for our most active specimen at 20° was therefore about $-10{\cdot}4°$, as compared with $-8{\cdot}3°$ for the purest acid of Fischer and Carl. Even after prolonged keeping in a vacuum, our acid could not be obtained in the solid form, so it was probably not quite optically pure.

Method of Experiment.

The method of experiment was similar to that already employed in the case of phenylchloroacetic acid (T., 1916, **109**, 1098). About 1 gram of the bromo-acid was dissolved in about 15 c.c. of the solvent, the solution saturated with dry ammonia, sealed up in a Jena-glass tube, and left at the ordinary temperature until the change was assumed to be complete. The solvent and excess of ammonia were then evaporated off at as low a temperature as possible (in some cases under diminished pressure), the residue was dissolved in water, made acid to Congo-red by addition of hydrochloric or hydrobromic acid, and the precipitate, consisting of the bulk of the imino-acid and cinnamic acid, collected and washed with cold water. From the precipitate, the pure imino-acid was isolated by extracting the cinnamic acid with ether.

The slightly acid aqueous filtrate containing the amino-acid, any unchanged bromo-acid, any hydroxy-acid or alkyloxy-acid formed in the course of the reaction, together with traces of imino-acid and cinnamic acid, was repeatedly extracted with ether, whereby all but the amino-acid and remaining imino-acid were removed. The

amino-acid was then freed from imino-acid and from ammonium chloride and bromide by evaporating the solution to dryness, dissolving in aqueous ammonia, again evaporating to dryness, and finally treating with small quantities of cold water until the filtrate was free from halogen salts. In this way, any remaining imino-acid was removed, since its ammonium hydrogen salt is stable and soluble in cold water.

The purity of the amino-acid was checked by determining its equivalent as hydrochloride, as described for phenylaminoacetic acid, and as in all cases practically theoretical results were obtained, it is unnecessary to quote the actual figures. In some cases the proportion of nitrogen was estimated by combustion.

As regards the different solvents, the results obtained with liquid ammonia, aqueous ammonia, and acetonitrile are of fundamental importance for the question of the replacement of halogen atoms by the amino-group, and the details of the experiments are therefore briefly summarised. As the remaining solvents, comprising a number of alcohols, all give very similar results, it seems unnecessary to describe the experiments in detail.

Aqueous Ammonia.

The velocity of reaction between inactive α-bromo-β-phenylpropionic acid and aqueous ammonia (35 per cent. NH_3) was determined approximately at 25°. From a solution containing 1·22 grams of the acid in 50 c.c. of the solution, about half the bromine was displaced in twenty-four hours. In a corresponding experiment with ethyl alcohol saturated with ammonia at 25°, about half the bromine was displaced in fourteen days.

In a preliminary experiment, in which 3 grams of the *r*-acid in 20 c.c. of aqueous ammonia (35 per cent. NH_3) was kept for seven days at 25°, 1·1 grams of pure *r*-phenylalanine and 0·1 gram of the imino-acid were obtained. The saturated solution of *r*-phenylalanine in water at 12° contains 1·24 grams in 100 c.c. of solution, about half that given by Fischer and Mouneyrat (*loc. cit.*) for the pure active forms.

A solution of 1·02 grams of *l*-α-bromo-β-phenylpropionic acid in 22 c.c. of aqueous ammonia (35 per cent. NH_3), kept for forty-two days at the ordinary temperature, gave 0·45 gram of amino-acid, $[\alpha]_D^{15} + 24°$ (m. p. 258—259° decomp.; rapid heating). In another experiment, 0·77 gram of the *l*-bromo-acid in dilute aqueous ammonia (4 per cent. NH_3), kept for twenty-one days at the ordinary temperature, yielded only 0·09 gram of amino-acid, $[\alpha]_D^{16} + 17°$. From the ethereal solution (compare the method of

experiment), crystals were obtained which, after recrystallisation from benzene, melted at 123—125° and gave in ethyl alcohol $[\alpha]^{16\cdot5}_{5461}$ $-21\cdot5°$, $c=0\cdot373$. The substance is evidently nearly pure *l*-α-hydroxy-β-phenylpropionic acid, formed by the action of water on the ammonium salt of the bromo-acid. It has been shown by McKenzie and Wren (T., 1910, **97**, 1355) that *l*-α-bromo-β-phenylpropionic acid gives a hydroxy-acid of the same sign when acted on by water, by aqueous sodium hydroxide, by water and calcium carbonate, and by water and silver oxide.

The effect of ammonium bromide on the activity of the resulting phenylalanine was determined as follows. A solution of 1·02 grams of the *l*-bromo-acid, $[\alpha]^{17}_{D}-8\cdot8°$, and 4 grams of ammonium bromide in 22 c.c. of aqueous ammonia (35 per cent. NH_3) was kept for eleven days at the ordinary temperature. The yield of phenylalanine was 0·27 gram of $[\alpha]^{13}_{D}+27°$, which is practically the same as that obtained in the absence of ammonium bromide.

Liquid Ammonia.

A solution of 0·53 gram of the *l*-bromo-acid, $[\alpha]^{17}_{D}-8\cdot8°$, in 16 c.c. of liquid ammonia, kept for fourteen days, gave 0·17 gram of amino-acid, $[\alpha]^{14}_{D}+8\cdot5°$. 0·85 Gram of the *l*-bromo-acid, $[\alpha]^{17}_{D}-8\cdot8°$, and 4 grams of ammonium bromide, dissolved in 13 c.c. of liquid ammonia and kept for fourteen days, gave 0·1 gram of amino-acid, $[\alpha]^{17}_{D}+24\cdot5°$. It appears from these data that in the presence of ammonium bromide the resulting phenylalanine is racemised to a much smaller extent than in the absence of the salt. In order to place this important result beyond doubt, two exactly parallel experiments were carried out, as follows. Two tubes, each containing 0·86 gram of the *l*-bromo-acid, $[\alpha]^{17}_{D}-10\cdot2°$, in 13 c.c. of liquid ammonia, and one containing 4 grams of ammonium bromide in addition, were kept for fourteen days. The ammonia was then allowed to evaporate, the residue in each case dissolved in water and made up to 50 c.c., and 4 grams of ammonium bromide were added to the solution which did not already contain the salt. The amino-acid was then isolated in the usual way. From the solution originally containing ammonium bromide, the yield of amino-acid was 0·12 gram, $[\alpha]^{10}_{D}+30°$. From the corresponding solution without ammonium bromide the yield of amino-acid was 0·14 gram, $[\alpha]^{10}_{D}+6\cdot5°$, so that the previous result was fully confirmed.

Acetonitrile.

A solution of 1·08 grams of the *l*-bromo-acid, $[\alpha]_D^{16} - 8{\cdot}8°$, in 15 c.c. of acetonitrile was saturated with dry ammonia at 9°, whereby the volume increased by 1·2 c.c. The solution at first was clear, but a precipitate consisting of the ammonium salts of the amino-acid, the imino-acid, and cinnamic acid soon began to form. After twenty-four days, the precipitate was collected, and the amino-acid obtained as usual, the yield being 0·2 gram, $[\alpha]_D^{14} + 9°$. The imino-acid was accidentally lost.

A second experiment with a less active bromo-acid ($[\alpha]_D^{18} + 5{\cdot}8°$) in more concentrated solution (3·9 grams in 17 c.c. of solvent), kept for twenty-one days, gave 0·35 gram of (recrystallised) phenylalanine, $[\alpha]_D^{20} - 8°$, and 0·57 gram of imino-acid (compare the section on the imino-acid). It appears therefore that, as would be anticipated, the more concentrated the solution of bromo-acid the greater is the yield of imino-acid.

The Alcohols.

As the reaction in these solvents is very slow, the solutions were kept for 280—300 days before separating the products. In each case, 0·7—0·8 gram of active bromo-acid was used, and the yield of amino-acid (except with benzyl alcohol) varied from 0·15—0·25 gram. With methyl alcohol, the solutions remained clear throughout, showing that the amino-acid and imino-acid (or their ammonium salts) are soluble in this solvent. With the other alcohols, except benzyl alcohol, a small amount of precipitate formed after a time. The absence of a precipitate in the benzyl alcohol solution is probably due to the slow rate of reaction in this solvent, as only 0·06 gram of amino-acid and 0·02 gram of imino-acid were obtained, although the mixture was kept for 309 days. The relative activities of the amino-acids from the different solvents are given in the table. The properties of the partly active imino-acids obtained from these solvents are briefly dealt with in the next section.

α-Imino-ββ-diphenyldipropionic Acid.

As this acid has not been previously obtained, it is desirable to describe its properties in some detail. Earlier experiments having shown that a good yield of the imino-acid was obtained from acetonitrile, 8·4 grams of the *r*-bromo-acid were dissolved in 20 c.c. of

this solvent, the solution being saturated with dry ammonia and kept for twenty-eight days. The precipitate was then collected, washed with ether, and the inactive imino-acid separated as already described (p. 158). After crystallisation from a mixture of acetone and water, in which it is very sparingly soluble, the compound forms stellar aggregates of elongated leaflets or needles melting and decomposing at 262—264°, with previous discoloration and shrinkage at 235°. Before analysis, it was dried for some hours at 100°:

0·2588 gave 0·6545 CO_2 and 0·1447 H_2O. C = 69·0; H = 6·27.
0·5561 „ 21·1 c.c. N_2 (moist) at 18° and 771 mm. N = 4·5.
$C_{18}H_{19}O_4N$ requires C = 69·0; H = 6·1; N = 4·5 per cent.

α-Imino-ββ-diphenyldipropionic acid is very sparingly soluble in water, practically insoluble in dilute or concentrated hydrochloric acid, but readily soluble in dilute alkali hydroxide solution. This shows that, as would be anticipated, it is an extremely weak base, whereas its acidic character is fairly pronounced. An attempt to determine its equivalent by evaporating with hydrochloric acid gave an unsatisfactory result, as the hygroscopic hydrochloride decomposed on drying at 100°. Further, no definite results for the equivalent were obtained by titration, using phenolphthalein as indicator, or by evaporating with ammonia, in an attempt to prepare a pure ammonium salt. Evidence was obtained in some of the experiments with acetonitrile as to the dibasic character of the acid, since the solid imino-acid compound which separates from this solvent during the reaction, on treatment with water in the cold, gives off ammonia, forming an ammonium salt (the hydrogen ammonium salt) soluble in water.

The amount of active imino-acid obtained from most of the solvents was very small, on the average 0·05 gram (from trimethylcarbinol 0·1 gram), but the rotation measurements were quite definite. The various specimens decomposed on heating to 245—251°.

Summary.

(1) The amino-acid obtained by the action of ammonia on optically active α-bromo-β-phenylpropionic acid in different solvents has in all cases the same sign, opposite to that of the original bromo-acid.

(2) The amino-acid from liquid ammonia and acetonitrile is more racemised than that from other solvents.

(3) The presence of ammonium bromide has little effect on the

activity of the product from aqueous ammonia; it greatly diminishes the racemisation when the reaction is carried out in liquid ammonia.

(4) α-Imino-ββ-diphenyldipropionic acid was isolated from the products of reaction in all solvents used, and its properties were investigated; the sign was in all cases the same as that of the original bromo-acid.

(5) The mechanism of displacement racemisation is discussed.

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CHEMISTRY DEPARTMENT,
BIRKBECK COLLEGE,
LONDON, E.C.

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XIX.—*The Action of Aniline on Carbon Tetrachloride.*

BY ERNST JOHANNES HARTUNG.

THE action of aniline on carbon tetrachloride was studied long ago by Hofmann (*Proc. Roy. Soc.*, 1858, **9**, 284). He found that no action was apparent at the ordinary temperature, but that, on heating 3 volumes of aniline with 1 volume of carbon tetrachloride in a sealed tube for thirty hours at 170—180°, a soft, black mass was obtained, from which he prepared pararosaniline and a new base, diphenylaminobenzamidine (carbotriphenyltriamine), $C_{19}H_{17}N_3$. He also obtained the hydrochloride of this substance, but did not pursue his researches further. Weith (*Ber.*, 1877, **10**, 358) many years afterwards attacked the problem of the structure of the base. He prepared it by Hofmann's method, and succeeded in showing (*Ber.*, 1879, **12**, 101) that the constitution could be represented as

$$C_6H_5\cdot N{:}C\begin{matrix}NH\cdot C_6H_5\\ C_6H_4\cdot NH_2\end{matrix}.$$

Later syntheses of diphenylaminobenzamidine (Michler and Walder, *Ber.*, 1881, **14**, 2174) confirmed the constitution thus established. The base is a product of the condensation of aniline with carbon tetrachloride, the latter supplying the central carbon atom. It is interesting in that the chlorine atoms of the tetrachloride have been displaced in three different ways: two chlorine

atoms have reacted with the two aminic hydrogen atoms in one aniline molecule, another has reacted with one aminic hydrogen atom in a second aniline molecule, and the fourth halogen atom has reacted with one of the ring hydrogen atoms in the para-position.

The present paper is the outcome of some experiments on the reaction in the presence of a catalyst. During the course of certain other work, it was noticed that a mixture of pure aniline and pure carbon tetrachloride, colourless at first, rapidly darkened at the laboratory temperature when in contact with a copper–mercury couple, ultimately becoming almost solid. As the reaction appeared to be far more rapid than that studied by Hofmann, it was of interest to discover whether the same products were formed. With this end in view, mixtures of aniline and carbon tetrachloride were allowed to react under varying conditions, and the main products were investigated.

Experimental.

Mixture 1.—A mixture of 3 molecular proportions of pure aniline and 1 molecular proportion of pure carbon tetrachloride was placed in contact with a copper–mercury couple and allowed to remain in a closed vessel until solid; this required three days at the ordinary temperature. Repeated extraction of the resulting black, oily substance with hot water showed that much of the original mixture was still unchanged. A tenacious black tar remained which solidified, on cooling, to a brittle, shining solid.

The brownish-red filtrate was boiled until all odour of aniline had disappeared, decolorised with animal charcoal, and set aside to crystallise. The crystals were purified by repeated crystallisation from water, and were then obtained quite clean and white, melting at 279° (291° corr.). This melting point agrees with that of the diphenylaminobenzamidine hydrochloride obtained by Weith. The presence of ionisable chlorine was shown by precipitation with silver nitrate; the base itself was prepared by the action of dilute sodium hydroxide solution on the salt and repeated crystallisation of the product from alcohol. It formed soft, creamy-white needles melting at 197° (203° corr.). (Found: C = 79·10; H = 6·16. $C_{19}H_{17}N_3$ requires C = 79·40; H = 5·97 per cent.) The substance was thus undoubtedly diphenylaminobenzamidine.

The black solid separated earlier was suspended in water and distilled in a current of steam. The distillate had a strong odour of phenylcarbylamine and deposited orange, crystalline scales.

These, after separation and purification, were shown to be azobenzene by their melting point, reactions, and quantitative analysis. A few drops of phenylcarbylamine were separated from the filtrate by extraction with ether.

Mixture 2.—This mixture was the same in composition as the previous one, and was heated at 80—90° with the copper–mercury couple under a reflux condenser for fifty minutes, when the mass had the appearance of moist black sand. Repeated extraction with hot water left only a small amount of dark, sooty material behind. The brown filtrate contained some aniline and azobenzene, and was boiled until these were removed. On crystallisation, much diphenylaminobenzamidine hydrochloride was again obtained. The red mother liquor, containing undoubtedly some pararosaniline hydrochloride, was evaporated, but the red colour was gradually destroyed, and only a further amount of the salt previously obtained and some aniline hydrochloride were found.

It was noticed that the diphenylaminobenzamidine salt obtained from this mixture had a persistent pale yellow colour, in spite of attempts to remove it by means of animal charcoal. Further, the corresponding salt from Mixture 1, which was pure white, became yellow on firm rubbing against the side of the porcelain dish with a glass rod, but ultimately became white again after some days. These changes could be induced repeatedly, so that apparently two modifications of the salt exist. On determining the melting point, the substance turns yellow at about 230°, and this colour increases until melting at 279° (291° corr.) takes place to a red liquid with partial decomposition.

Mixture 3.—This was a mixture of about equal parts of aniline and carbon tetrachloride, part of which was the middle fraction in the separation of the two liquids by fractional distillation. It was allowed to remain for several months without heating and in the absence of the catalyst. At intervals of a few weeks, the crystals which had formed in the dark brown liquid were collected and the filtrate was returned to the bottle. In each case, the substance obtained was treated as follows: The felted, hair-like mass was pressed in absorbent paper, extracted with water, and the extract allowed to crystallise. When crystals appeared, they were purified and identified as diphenylaminobenzamidine hydrochloride. The insoluble residue was crystallised repeatedly from alcohol and obtained in pure white needles melting at 238° (246° corr.). The substance contained no chlorine and formed no salts. (Found: C = 73·46; H = 6·04· N = 13·3. $C_{13}H_{12}ON_2$ requires C = 73·6; H = 5·7; N = 13·2 per cent.) The solubility and general relations indicated *s*-diphenylcarbamide.

An interesting point noticed was that for some weeks after the reaction in the mixture had been proceeding, the separated substance contained scarcely any diphenylaminobenzamidine salt, but consisted almost entirely of the carbamide. After several months, however, the separated solid contained little of the carbamide and consisted mostly of the salt, showing that the latter forms only slowly. The formation of diphenylcarbamide is interesting; probably a dichloro-compound, $CCl_2(NHPh)_2$, is formed first, which is then hydrolysed by water, either present originally in the mixture or entering subsequently from the air. That the water was present at the beginning is indicated by the gradual falling off in the production of the substance as the experiment was prolonged.

Mixture 4.—This was a mixture containing a very large excess of carbon tetrachloride; it consisted of the first fraction in the separation of carbon tetrachloride and aniline by fractional distillation, to which a small amount of aniline had been added. On keeping in a closed bottle, it gradually became brown, and, after two months, deposited a mass of crystals, some having a deep blue colour. No catalyst was added.

The separated substance proved to be a complex mixture of several different compounds. After many trials, the following scheme of separation was adopted: The whole mass, weighing about 5 grams, was extracted repeatedly with light petroleum in a Soxhlet apparatus for several hours. The brown extract gave on evaporation a few milligrams of dark solid which, when crystallised from carbon tetrachloride, appeared in very small, reddish-brown prisms melting at 237° (245° corr.). It was insoluble in water, dilute acids, or alkalis, and could not be identified. The substance in the Soxhlet tube was extracted repeatedly with ether, leaving behind a dark blue residue. The ethereal extract was found to contain diphenylcarbamide, which was separated and purified. The blue residue contained at least two substances, and many solvents were tried without any success in separating them. This was finally accomplished by fractional sublimation under diminished pressure. Much aniline hydrochloride sublimed, leaving a few milligrams of dark blue solid behind.

The blue substance contained carbon, hydrogen, nitrogen, and chlorine; it dissolved in water, alcohols, and other solvents, giving deep blue solutions. With sodium hydroxide, it gave a pink solution, the colour rapidly disappearing on boiling. This would indicate possibly a basic dye. Direct dyeings on silk, wool, and cotton were made. On silk, the colour was a deep purple blue, scarcely affected by exposure to sunlight or by washing in weak acids or alkalis. On wool, the dyeings were deep grey blues, fast

to light, and resisted boiling in soapy water fairly well. The results on cotton were poor, even with mordants. Attempts to identify the dye were not successful, and no investigation of the constitution could be undertaken on account of the very small amount available.

A small quantity of azobenzene was obtained from the mother liquors of Mixture 4 after removal of the crystals which had formed.

The results of the investigation may be summarised as follows: Previous observations by Hofmann and others have shown that carbon tetrachloride and aniline react slowly together at 180° giving diphenylaminobenzamidine and pararosaniline. It is now found that this action takes place very slowly at the ordinary temperature, the products varying with the original mixture and the conditions. Neglecting the brown discolorations soon appearing, the first product, after some weeks' action, seems to be *s*-diphenylcarbamide, produced by the hydrolysis of a dichloro-substitution product of carbon tetrachloride by small amounts of water present in the reaction mixture. The formation of diphenylaminobenzamidine is a slower process and takes some months. In solutions of certain composition, small quantities of coloured products may be obtained, the formation of which is probably indirect. Two such products have been isolated in the pure state, one in minute brown crystals and the other as a deep blue substance with dyeing properties.

In the presence of a copper–mercury couple, the reaction is comparatively rapid. At the ordinary temperature, a small amount of pararosaniline is formed, as well as phenylcarbylamine and a fair amount of azobenzene. The main product is, however, diphenylaminobenzamidine hydrochloride. At 80—90°, the reaction is rapid, the product consisting of the diphenylaminobenzamidine salt with some small amount of pararosaniline. In all cases, however, the reaction is not completed, and only the main constituents of the very complex mixtures have been identified. It would appear from the results of Hofmann and Weith as to the formation of pararosaniline that the yield of this substance is favoured by increasing the temperature, it possibly being formed by intramolecular rearrangement from the isomeric diphenylaminobenzamidine. Some experiments were made to convert this base into the dye by raising the temperature in the presence of various substances, but without success.

The use of the copper–mercury couple makes the preparation of diphenylaminobenzamidine from aniline and carbon tetrachloride a simple matter, and a fair yield is obtained. Further, as both

aniline and carbon tetrachloride are characteristically type substances, the range of action of this catalyst will probably be extensive in reactions between related compounds.

My sincere thanks are here expressed to Professor Orme Masson for his continued interest in, and kindly criticism of, this work.

Chemistry Department,
University of Melbourne. [*Received, October 1st*, 1917.]

XX.—*The Synthesis of Ammonia at High Temperatures.*

By Edward Bradford Maxted.

If the equilibrium between nitrogen, hydrogen, and ammonia be examined thermodynamically, it will be seen that whereas at moderate temperatures, such as are employed for the catalytic synthesis of ammonia, an increase in temperature leads to a rapid decrease in the amount of ammonia in equilibrium with nitrogen and hydrogen, this amount passes at higher temperatures through a minimum and, with increasing temperature, begins to rise with increasing velocity.

For a rough preliminary calculation, either of the following formulæ, which have been worked out by Haber (*Zeitsch. Elektrochem.*, 1914, **20**, 597; "Thermodynamics of Technical Gas Reactions," p. 204) for the ammonia equilibrium at temperatures below 1000°, may be extended to higher temperatures in order to demonstrate this reversal, but it will be shown that more ammonia is actually obtained at, for instance, the temperature of the oxyhydrogen flame than can be accounted for by either formula

We have, accordingly, if $K = \frac{P_{NH_3}}{P_N^{\frac{1}{2}} \times P_{H_2}^{\frac{3}{2}}}$.

(*a*) $\log_{10}K_p = 2215/T - 3{\cdot}625\log_{10}T + 0{\cdot}000307T + 0{\cdot}29 \times 10^{-6}T^2 + 4{\cdot}82$.

(*b*) $\log_{10}K_p = 2098/T - 2{\cdot}5088\log_{10}T - 0{\cdot}0001006T + 0{\cdot}186 \times 10^{-6}T^2 + 2{\cdot}1$.

The calculated variation of K with temperature is given in the following table.

TABLE I.

Temperature.	Value of $K \times 10^4$. By equation (a).	By equation (b).
1000° Abs.	5·7	5·7
2000	0·78	0·26
3000	3·03	0·28
4000	152·0	1·5

It was accordingly to be assumed that mixtures of nitrogen and hydrogen, at high temperatures, contain ammonia which by rapid cooling might be brought, without complete decomposition through the temperature zone at which ammonia becomes unstable into that region of temperature in which it is once more capable of stable existence.

The subject has been examined experimentally, first for not extremely high temperatures, by rapidly cooling mixtures of nitrogen and hydrogen from the temperature of the oxy-hydrogen flame to the ordinary temperature, yields of ammonia amounting to more than 1 per cent. by volume under atmospheric pressure being obtained. The result is of special interest if one considers that such a yield is only possible otherwise below 350°, a temperature at which the formation of ammonia, even in the presence of catalysts, does not proceed with measurable velocity.

The method of heating and suddenly cooling employed in the work about to be described consists in injecting the mixture of nitrogen and hydrogen into an oxy-hydrogen flame burning under water, or, in a second series of experiments, into an oxy-hydrogen flame burning in a water-cooled silica tube, the amount of ammonia formed being estimated in some cases by direct titration with $N/10$-acid and in others colorimetrically by Nessler's solution. The reaction mixture contained, therefore, in addition to nitrogen and hydrogen, a volume of steam depending on the proportion of the mixture of nitrogen and hydrogen injected into the flame. It was noted, further, that the yield of ammonia recovered at the ordinary temperature was considerably greater when direct cooling with water was employed than when the flame was cooled by contact with a water-cooled quartz tube.

EXPERIMENTAL.

For the first series of experiments, the reaction chamber consisted of a silica tube 6·5 mm. in diameter and 7·5 cm. long, completely immersed in about 900 c.c. of distilled water contained in a glass vessel fitted with an efficient glass cooling coil through which

a rapid current of water was passed, the vessel having a capacity of slightly more than 1 litre. Into the quartz reaction chamber, nitrogen, hydrogen, and oxygen, at rates determined by velocity meters, were injected and ignited, the flame gases passing out of the open end of the reaction chamber and bubbling through the water, by the action of which the ammonia, recovered from the flame by sudden cooling, was retained. In some cases the water was replaced by dilute acid, without, however, any appreciable difference in the results, provided that the water was kept cool. The amount of oxygen passed into the reaction chamber was in every case regulated in such a way as to leave uncombined hydrogen equal to three times the volume of the nitrogen passed in.

In order to make a comparison of the results obtained at various temperatures and at varying partial pressures, that is, by the increasing dilution of the oxy-hydrogen flame with a mixture of nitrogen and hydrogen, advantage was taken of the known fact that for small percentages of ammonia the volume formed at a given temperature is directly proportional to the pressure, so that the volume of ammonia which would be formed at the temperature of the flame but under atmospheric pressure may be calculated by dividing the value observed by the corresponding partial pressure of the nitrogen, hydrogen, and ammonia in the nitrogen, hydrogen, ammonia, and steam reaction mixture. In this way, it becomes possible easily to compare the relative amounts of ammonia formed at different temperatures and under varying partial pressures. In this series of experiments, the ammonia in the resulting solution was estimated colorimetrically by Nessler's reagent, care being taken to use distilled water free from ammonia for cooling the flame. In those cases in which dilute acid was used for cooling, this was made up by dissolving 40 c.c. of ammonia-free $N/10$-sulphuric acid in each litre of distilled water.

Table II summarises the results obtained by direct cooling with water or dilute acid.

It will be noticed that the percentage of ammonia by volume in the mixture of nitrogen and hydrogen recovered by suddenly cooling (reduced for uniformity to one atmosphere pressure) rises from 0·0027 to 1·23 as the reaction temperature approaches that of the oxy-hydrogen flame. The flame temperatures are calculated from Féry's observed values for the oxy-hydrogen and air-hydrogen flames.

Experiments with Indirect Cooling.

The reaction chamber employed for this series of experiments consisted of a vertical quartz tube 90 cm. long and 8 mm. in

TABLE II.

No. of expt.	Velocity in litres per hour of gases passed into reaction chamber.			Duration of expt. in minutes.	Cooling agent.	Percentage by volume of ammonia in mixture of nitrogen and hydrogen.	Partial pressure of system nitrogen–hydrogen–ammonia in flame.	Estimated temperature of flame. ° Abs.	Percentage volume of ammonia formed at absolute pressure of 1 atm.
	Nitrogen.	Hydrogen.	Oxygen.						
1	60	220	20	15	Acid	0·00235	0·86	1280	0·0027
2	60	260	40	15	Water	0·005	0·75	1500	0·0067
3	60	360	90	15	Water	0·013	0·57	1830	0·023
4	30	270	90	15	Water	0·018	0·4	2120	0·045
5	20	240	90	15	Water	0·0205	0·31	2260	0·066
6	20	300	120	10	Acid	0·0366	0·25	2350	0·146
7	20	460	200	5	Acid	0·07	0·167	2470	0·42
8	10	430	200	5	Acid	0·112	0·091	2580	1·23

internal diameter. This was cooled by making it the inside tube of a long Liebig's condenser. The flame gases, which in this case were cooled only by contact with the cold walls of the silica tube, were allowed to pass from the bottom of the tube through a known quantity of $N/10$-acid, which was afterwards titrated with alkali in the usual manner. As was to be expected from the less rapid cooling, the amount of ammonia produced at high temperatures was less than that obtained by directly leading the flame into cold water. At lower temperatures, the divergence became less marked until, at the lowest temperature studied, approximately equal values for the yield of ammonia were observed. The results obtained by indirect cooling in the above manner are summarised in table III.

TABLE III.

No. of expt.	Duration in minutes.	Partial pressure of system nitrogen–hydrogen–ammonia in flame.	Percentage by volume of ammonia in mixture of nitrogen and hydrogen.	Estimated temperature of flame. ° Abs.	Percentage volume of ammonia at absolute pressure of 1 atm.
1	30	0·86	0·0026	1280	0·003
2	30	0·57	0·0068	1830	0·012
3	30	0·25	0·0134	2350	0·054
4	30	0·167	0·0196	2470	0·118
5	30	0·091	0·019	2580	0·21

Summary.

It may be shown thermodynamically that the ammonia equilibrium first sinks with increasing temperature, then passes through a minimum, and finally rises again. By suddenly cooling mixtures of nitrogen and hydrogen, much of the ammonia contained therein may be obtained at the ordinary temperature, and the ammonia formed is, if we assume Féry's measurements for the temperature of the oxy-hydrogen flame to be correct, greater than corresponds with Haber's equation for the ammonia equilibrium at temperatures below 1000°. With direct cooling of flames by means of water, volumes of ammonia amounting for atmospheric pressure to 1·23 per cent. of the mixture of nitrogen and hydrogen have been obtained. With indirect cooling, less ammonia is recovered, the maximum volume per cent. obtained at atmospheric pressure being 0·21.

GAS DEVELOPMENTS, LTD.,
WALSALL.

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XXI.—*A Reinvestigation of the Cellulose–Dextrose Relationship.*

By Mary Cunningham.

It has been assumed that in order to determine the structure of the cellulose molecule, an obvious course is to identify quantitatively the products of ultimate hydrolysis and from their known constitution to reconstruct the original complex. Hence the commonly accepted view of (cotton) cellulose as a polydextrose anhydride. Recent researches have, however, cast doubt on such interpretation of the results of hydrolytic resolution, for they have shown that a molecular structure is not necessarily that of its constituents after hydrolysis (Fischer, *Ber.*, 1914, **47**, 1980; Irvine, Fyfe, and Hogg, T., 1915, **107**, 524; Haworth and Law, T., 1916, **109**, 1314). Moreover, and particularly as regards cellulose, observations of optical activity and reducing power of the products of resolution have been accepted as unquestionable evidence of identification, whilst the isolation of the substances having the recorded constants has even been regarded as superfluous. It seemed important, therefore, on this basis of criticism to reinvestigate the products formed from cellulose by the action of acids which have usually been regarded as giving maximum resolution, namely, sulphuric acid dihydrate, $H_2SO_4,2H_2O$, and hydrochloric acid of more than 40 per cent. concentration.

Two classes of cellulose have been selected for experiment, namely, cotton cellulose as the normal type, and esparto cellulose, which is characterised by a high furfuroid content, resembling in this respect the cereal celluloses, but being more resistant to hydrolysis. In the case of cotton cellulose, particular attention has been paid to the action of 40 per cent. hydrochloric acid, as the behaviour of the normal cellulose to sulphuric acid has already been studied by numerous investigators (compare Flechsig, *Zeitsch. physiol. Chem.*, 1883, **7**, 523; Stern, T., 1895, **67**, 74; and Ost and Wilkening, *Chem. Zeit.*, 1910, **34**, 461). Esparto cellulose has not, however, previously been examined in this respect, but it has now been found that treatment with 73 per cent. sulphuric acid results in the formation of polysaccharose esters, which were usually obtained as barium salts. These compounds bear sufficient relation to the original complex to give a high, although diminished, yield of furfuraldehyde on distillation, but they are distinguished from the cotton cellulose sulphates prepared by Stern (*loc. cit.*), by the action of concentrated sulphuric acid, in having a much smaller

content of inorganic material. In the esparto products, the proportion of barium combined is approximately equal to that of SO_4, so that the two are present in the ratio $Ba_2:(SO_4)_3$. This means that if either neutral or acid sulphates or both are formed with alcoholic hydroxyl groups, then an excess of barium is present which must be in union with hydroxyl groups of a sufficiently acid character to decompose barium carbonate, whilst the acid character of these hydroxyl groups is further emphasised by the stability of the compounds towards carbon dioxide, and this establishes them as genuine barium salts. The SO_4 residues are also in very stable union, as complete precipitation can only be effected by boiling with concentrated hydrochloric acid in the presence of barium chloride for some hours, and although alkaline hydrolysis with barium hydroxide solution greatly increases the barium content, the SO_4 groups are not entirely removed, and it is quite possible that some of them are present in the form of a neutral ester.

As regards hydrolysis by the action of 40 per cent. hydrochloric acid, the claim has been put forward that cotton cellulose under these conditions is quantitatively resolved into dextrose. It must be remembered, however, that this conclusion and the theoretical considerations to which it obviously leads were based, not on the yield of dextrose actually isolated, but, by inference, on the specific rotation and reducing power of a 1 per cent. solution of cellulose in the acid,* the yield of dextrose being calculated from the formula $c = \alpha \times 100/[\alpha]_D$, where $[\alpha]_D$ is the specific rotation of dextrose in 40 per cent. hydrochloric acid (Willstätter and Zechmeister, *Ber.*,

* Willstätter and Zechmeister appear to have overlooked the elaborate investigation of J. König, and F. Hühn, "Bestimmung der Zellulose" (Berlin, 1912). In investigating celluloses isolated by the several hitherto recognised standard methods (Hugo Müller, Cross and Bevan, König, Tollens, Schulze, etc.) they employ the method of solution in the zinc chloride–hydrochloric acid reagent (Cross and Bevan) and polarimetric observations of the solutions. In this reagent, dextrose was found to have a maximum $\alpha_D + 60°$ and xylose $+32°$.

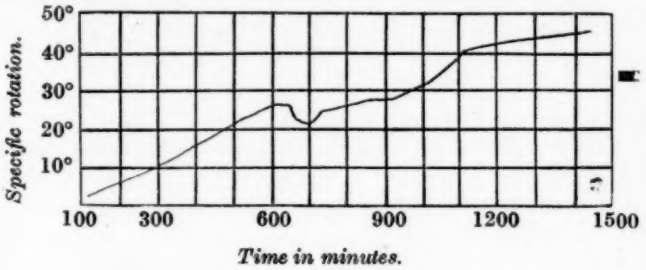
Comparing these solutions of the celluloses (derivatives) there is a maximum for α_0 of $+82{\cdot}5°$ in the case of cotton cellulose "purified" by the König method; the maxima are very variable over the special range of products investigated.

These authors do not draw the conclusion that dextrose is formed as such, or that the rotations, although apparently specific, are attributable to ultimate groups, namely, hexose (or pentose). What they state is that maximum of rotation is a criterion of maximum "purity" of cellulose. This conclusion has been examined in a communication dealing critically with the whole paper (Cross and Bevan: *Eighth Int. Congr. App. Chem.*, 1912, **13**, 101). No doubt attaches to their experimental numbers and, being directly relevant to the issue raised by Willstätter and Zechmeister, they have to be taken into consideration.

1913, **46**, 2401). Such data seemed entirely inadequate in view of the fundamental character of the issues involved, and it was therefore decided to repeat the polarimetric observations * and also to isolate the products in solution after definite intervals of

FIG. 1.

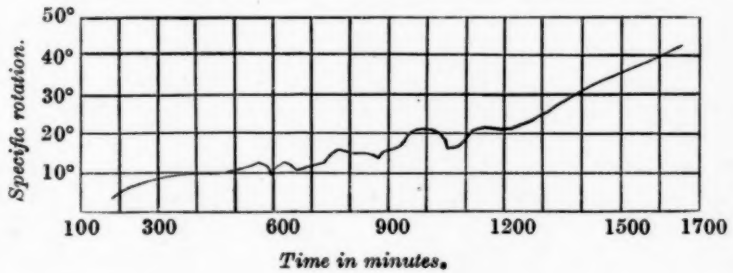
Hydrolysis of cotton cellulose with 40 per cent. hydrochloric acid.



time. The changes in optical activity were observed as nearly as possible every 30 minutes for 24 hours, and the results are shown graphically in Figs. 1 and 2. It will be observed from Fig. 1 (cotton cellulose) that there is a continuous increase in

FIG. 2.

Hydrolysis of esparto cellulose with 40 per cent. hydrochloric acid.



activity up to 600 minutes, but then a marked fall occurs, followed by a fairly regular rise to the value $[\alpha]_D$ +45·6° at the end of 1400 minutes, with a further increase of 10° during the next 13 hours.

* The polarimetric observations were made after dilution, owing to the doubtful condition of sugars when dissolved in strong acids. Mutarotation to the α-form assumed by Willstätter is not a satisfactory explanation of the remarkable increase in activity observed, for dextrose shows in acid containing 44·5 per cent. of hydrogen chloride a specific rotation 60° above that of the α-isomeride, and this suggests more profound constitutional change than merely isomeric transformation.

Esparto cellulose (Fig. 2) showed for the most part similar fluctuations in rotation, but the initial attack of the acid is less delayed, whilst more irregularities occur in the middle portion of the curve, and the final value for the specific rotation is somewhat lower. The hydrolytic solutions were diluted and neutralised at the end of 24 hours, when the esparto solution gave $[\alpha]_D$ +41·1° and the cotton cellulose solution 45·6°, but in the latter case a separation of the products was also made at the end of 48 hours, since the specific rotation had risen to the value 56·5°, which is very nearly that of dextrose calculated according to the equation

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$

The substances so prepared were lead salts of polysaccharose esters similar to the barium salts previously described, the higher molecular proportion of chlorine entering into combination according with the superior esterifying power of hydrochloric acid as compared with sulphuric acid. Dextrose could not be identified in any of the fractions, and, if present, it would appear and be concentrated in the more readily soluble portions, but these show a higher inorganic content and a lower specific rotation. The possibly misleading character of polarimetric observations when unsupported by the full identification of products is also emphasised by the fact that whilst solutions of the very divergent types of cellulose investigated show almost concordant optical activity, the esparto products are furfuroids, and their solution gives, throughout the hydrolysis, high yields of furfuraldehyde with a final loss of only 3 per cent., even if neutralisation is postponed for six days. Further, dextrose is not formed on subsequently heating the salts with dilute acid. Both the sulphates and the chlorides so treated show a fall in optical activity, whilst the products, isolated after the rotation has become constant, contain a diminished quantity of inorganic material, and, in the case of esparto, give a smaller yield of furfuraldehyde on distillation. Evidently, therefore, the main action of the acid is to cause further condensation of the original complex, and not hydrolysis to sugar. The same is even true of a sulphate prepared free from barium by the action of cold sulphuric acid on an alcoholic solution of the salt. It should be mentioned, however, that by the sulphuric acid hydrolysis of the barium salts, residual syrups are obtained which give glucosazones in small yield. The ester salts are further characterised by a marked reducing power and also by showing slight mutarotation which is uniformly downwards. These observations indicate that the compounds are correctly described as ester salts of polysaccharoses, and it is possible that they represent the initial results

of hydrolysis and are not "reversion products" (Ost and Wilkening, *loc. cit.*), as otherwise the fluctuations in optical activity would have been more marked. On the other hand, the main result of these experiments, that no quantitative resolution of cellulose to dextrose is in reality obtainable, reopens the whole question of the structure of the complex. This aspect of the matter is, however, dealt with in the following paper by Messrs. Cross and Bevan.

Experimental.

The Action of Sulphuric Acid Dihydrate, $H_2SO_4,2H_2O$, *on Esparto Cellulose.*—Sixty grams of cellulose, dried at 80°, were mixed with 300 c.c. of 73 per cent. sulphuric acid in a stoppered bottle. The bottle was mechanically shaken for six hours, and the very viscous solution allowed to remain for a further 18 hours, when it was diluted with 2 litres of water. A very small amount of regenerated cellulose was obtained, and the excess of sulphuric acid was removed by the addition of barium carbonate, followed by filtration. The syrup left after concentration of the filtrate was dissolved in 50 per cent. alcohol, and from this solution, after filtering, 37 grams of a white, amorphous product were obtained by the addition of 80 per cent. alcohol, whilst 8 grams of a second fraction were precipitated from the filtrate by means of absolute alcohol. Both fractions were very deliquescent and were only prepared in a solid form with difficulty. Drying operations had to be carried out at 50—60°, as charring easily took place, and the excessive swelling which accompanied it rendered elementary analysis impossible.

Fraction I.—Found: Ba = 8·6; SO_4 = 7·9; $C_5H_4O_2$ (furfuraldehyde) = 8·3. $[\alpha]_D$ +47·8° to 45·5°.

Fraction II.—Found: Ba = 8·6; SO_4 = 10·6; $C_5H_4O_2$ = 8·0 per cent. $[\alpha]_D$ +55·3° to 51·6°.

Preparation of an Ester Free from Barium.—In attempting to isolate an ester free from barium, it was desired to avoid any further hydrolysis of the original product, and therefore the barium salt remained in acid alcoholic solution for some days in the cold. Barium sulphate was then removed by filtration, and the addition of absolute alcohol to the filtrate gave a white, amorphous precipitate entirely free from ash.

Found: SO_4 = 5·3; $C_5H_4O_2$ = 6·2 per cent. $[\alpha]_D$ +41·6°.

Hydrolysis of Barium Salt with 2 per cent. Sulphuric Acid.—An 8·5 per cent. solution of the barium salt was made up in 2·3

per cent. sulphuric acid, and the following changes in optical activity were observed:

Initial specific rotation	42·3°
After heating at 100° for 20 minutes	34·5
" " " " 40 "	32·8
" " " " 100 "	30·8 (constant)

At this stage in the hydrolysis, the acid solution was neutralised with barium carbonate, and after concentrating the filtrate, the syrupy residue was dissolved in 50 per cent. alcohol, and the solution gave a white, amorphous precipitate on the addition of absolute alcohol. The yield only amounted to 60 per cent.

Found: Ba = 5·3; SO_4 = 6·0; $C_5H_4O_2$ = 5·0 per cent $[\alpha]_D$ +33·8°.

Hydrolysis of Barium Salt with 5 per cent. Barium Hydroxide Solution.—The barium salt was heated at 100° with the alkali for 7 hours. An immediate precipitation of barium sulphate occurred, but the resulting compound, isolated as usual, still contained a small percentage of SO_4. The barium content was greatly increased, and this probably indicates the presence of hydroxyl groups in the original complex, sufficiently acidic to combine with barium, but not able to decompose barium carbonate. The compound was too dark for polarimetric observations.

Found: Ba = 25·1. SO_4 = 2·4 per cent.

The Action of 40 per cent. Hydrochloric Acid on Cotton Cellulose. (a) *Changes in Optical Activity.*—A 5 per cent. solution of cotton cellulose in 40 per cent. hydrochloric acid was prepared, and the polarimetric readings were taken after the concentration had been lowered to 1 per cent. This gives an acid concentration of 8 per cent., in which, as shown by Willstätter, the specific rotation of dextrose is practically normal. The readings at 15°, from which the foregoing curve was constructed (Fig. 1), are given below.

Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.
120	3·2°	385	14·8°	635	26·0°	900	28·4°	1245	42·4°
150	3·2	415	16·4	675	22·4	930	29·2	1290	44·0
180	5·6	455	19·2	705	22·4	1010	32·8	1330	44·8
210	6·0	485	20·0	735	25·2	1040	34·8	1375	44·8
240	8·0	515	21·6	765	24·8	1070	37·6	1400	45·6
295	10·4	545	22·4	795	26·4	1100	39·2	1435	45·6
325	11·2	575	24·2	825	27·6	1160	40·8	2250	56·8
355	12·8	605	26·0	870	28·0	1195	41·6		

It will be seen that, except for some irregularities in the period 635 to 825 minutes, the optical activity continuously increases to the final value +56·8° at the end of 2250 minutes. The values for $[\alpha]_D$ are calculated on the original weight of cellulose.

(b) *Yield of Furfuraldehyde.*—At the end of 24 hours, the acid solution was diluted to 12 per cent. and distilled, as in the ordinary procedure for a furfuraldehyde estimation. The yield only amounted to 1·2 per cent., calculated on the original weight of cellulose, so that evidently the high furfuroid content of the esparto solution is due to the persistence of the original complex and not to any specific action of the acid treatment.

(c) *Isolation of the Products formed after Hydrolysis for* (1) 24 *Hours*, (2) 48 *Hours.*—When the specific rotation had reached the value +45·6° at the end of 24 hours, the acid solution was diluted to 1 litre and neutralised with lead carbonate. The filtrate was then concentrated under diminished pressure, and the syrupy residue freed from any lead chloride retained as impurity by precipitation with hydrogen sulphide and subsequent neutralisation with silver carbonate. Some lead sulphide was formed, but very little acidity developed, and it is therefore possible that a portion of the precipitated lead was in combination with an organic compound. After further concentration in a vacuum, a clear, colourless syrup was obtained which dissolved readily in 80 per cent. alcohol, and the addition of absolute alcohol precipitated from it 2·5 grams of a white, amorphous, deliquescent compound. A second fraction was obtained from the filtrate amounting to 3·1 grams, and there then remained 1·3 grams of residual syrup, which also contained lead and chlorine. The total yield of products is therefore only 69 per cent.

Fraction I.—Found: Pb = 7·9; Cl = 6·1; $C_5H_4O_2$ = 1·08. $[\alpha]_D$ +48·2° to 43·0°.

Fraction II.—Found: Pb = 8·2; Cl = 7·3 per cent. $[\alpha]_D$ +46·7° to 33·4°.

(2) *Products Formed after* 48 *Hours' Hydrolysis.*—The products in solution after the more prolonged hydrolysis were separated as previously described, but their general characteristics were quite similar, although the specific rotation of the acid solution had increased to the constant value +56·8°. The yields from 10 grams of cellulose were: fraction I, 2·1 grams; fraction II, 3·9 grams with 0·9 gram of residual syrup, also containing lead and chlorine.

Fraction I.—Found: Pb = 8·3; Cl = 6·2. $[\alpha]_D$ +42·5° to 34·5°.

Fraction II.—Found: Pb = 9·4; Cl = 9·8 per cent. $[\alpha]_D$ +26·7° to 17·3°.

The Action of 40 *per cent. Hydrochloric Acid on Esparto Cellulose.* (a) *Changes in Optical Activity.*—A 5 per cent. solution of esparto cellulose was prepared as previously described in the case of cotton cellulose. The esparto solution darkened more quickly

and the precipitated cellulose was more discoloured. The darkening of the solution was due to the separation of humus substances which were not entirely soluble in alkali. The polarimetric observations were taken as before, at 15°, after dilution to 1 per cent. concentration, reckoned on the original weight of cellulose.

Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.
130	8·4°	460	22·4°	750	30·4°	990	35·0	1330°	39·2°
155	9·2	490	24·8	780	29·6	1030	34·4	1405	40·0
185	9·6	535	26·8	810	29·6	1075	37·6	1490	41·1
215	10·8	570	27·2	840	30·4	1135	39·2	1620	46·3
245	11·6	600	28·4	870	32·0	1165	38·4	1770	45·6
290	13·6	630	29·2	900	31·2	1200	40·0	2035	46·3
320	15·2	670	31·2	930	35·1	1230	38·4	2250	46·3
370	18·0	735	32·4	960	35·0	1295	39·2	3000	54·4
400	19·6								

It will be seen that for the most part the changes in optical activity are parallel to those recorded in the case of cotton cellulose.

(b) *Variations in Yield of Formaldehyde.*—The yield of furfuraldehyde was determined at definite intervals by distilling a portion of the acid solution after the acid concentration had been reduced to 12 per cent.

Time from start.	$[\alpha]_D$.	Yield of furfuraldehyde, per cent.
12 hours	29·5°	11·6
24 „	41·4	11·6
6 days	49·6	9·9

The yield of furfuraldehyde is calculated on the original weight of cellulose dissolved.

(c) *Isolation of the Products of Hydrolysis.*—At the end of 24 hours, the acid solution was treated as described under cotton cellulose. The products contained a complex which yielded furfuraldehyde, but otherwise they had the same general characteristics. As usual, drying operations had to be conducted with great care, as charring easily occurred, accompanied by marked swelling, which rendered an elementary analysis impossible.

Fraction I.—Found: Pb = 7·9; Cl = 5·6. $[\alpha]_D$ + 30·5° to 22·2°.

Fraction II.—Found: Pb = 8·2; Cl = 8·6; $C_5H_4O_2$ = 5·7 per cent. $[\alpha]_D$ + 32·2° to 25·2°.

The total yield was only 40 per cent. of the weight of cellulose employed.

Summary and Conclusions.

(1) The products of hydrolysis of the celluloses are not identifiable by the rotation constants of the hydrolytic solutions. The latest conclusions as to the cellulose–dextrose relation, based on

optical data, are now shown to be invalidated, for the following reasons: (*a*) Such widely different types as cotton and esparto celluloses give identical optical data on hydrolysis, but the ultimate products have necessarily divergent constitutions. (*b*) Solution in concentrated hydrochloric acid produces constitutional changes even in the simple hexoses of known configuration, as shown by the marked fluctuations in optical activity accompanying slight variations in acid concentration. The products obtained in acid solution from cellulose may therefore be the result of several concurrent reactions. Even when these are reduced to a minimum by sufficient dilution, there is still the ascertained complication of esterification.

(2) No quantitative resolution of cellulose to dextrose has yet been obtained, and the claim made by Willstätter and Zechmeister to have effected this conversion, since it rested solely on polarimetric observations and the equally non-specific data of cupric reduction, would seem inadmissible.

(3) Isolation and identification of the products of hydrolysis or their immediate and characteristic derivatives must be regarded as the only trustworthy means of quantitatively studying the resolution of highly complex colloidal carbohydrates such as cellulose.

(4) Under the action of both sulphuric and hydrochloric acids, cellulose forms esters of polysaccharoses which contain acidic hydroxyl groups. In the case of hydrolysis by the latter acid especially, attempts to isolate dextrose, if present, by fractionation only resulted in the production of compounds having a higher content of inorganic material and a lower specific rotation, whilst the effect of subsequent heating with dilute acid is to produce, not hydrolysis, but further condensation.

I wish to express my indebtedness to the Carnegie Trustees, who provided the opportunity for carrying out this research, also to Professor J. C. Irvine and Mr. C. F. Cross, who have given me valuable advice, and, lastly, to Messrs. Tullis, Russell and Company, who kindly supplied the esparto products used in the experiments.

The United College of St. Salvator and St. Leonard,
Chemical Research Laboratory,
The University,
St. Andrews. [*Received, February 7th,* 1918.]

XXII.—*Esparto Cellulose and the Problems of Constitution.*

By Charles Frederick Cross and Edward John Bevan.

The study of cellulose by way of processes of "solution" and of its ester derivatives through their solutions has extended rather than deepened our knowledge of cellulose matter; for progress in the more fundamental regions there are required (*a*) a comprehensive study of physical constants and (*b*) an exhaustive study of processes and products of resolution. We have devised a plan of investigation towards these ends, and in the former (*a*) we are joined by S. S. Napper and S. J. Lewis; Dr. Lewis has made substantial progress in measuring fluorescence effects, absorption spectra, diathermancy, but more especially density-volume phenomena, the results of which promise to throw light on fundamental points. These researches will be the subject of future communications.

The latter (*b*) specially sets out from a critical survey of the evidence for the generally accepted view of cellulose as a polyhexose anhydride, that is, with ultimate groups of configuration conforming closely with that of dextrose. In this critical study and in the resulting scheme of experimental revision of the accepted evidence—based on resolutions assumed to be purely hydrolytic—we are joined by Professor J. C. Irvine, in whose laboratory the work described by Miss Cunningham in the preceding paper has been carried out.

The selection of esparto cellulose as a type for parallel study with the normal cotton cellulose is justified by considerations a priori and by the results of our own further study of this product undertaken concurrently.

(1) Esparto cellulose presents striking divergences from the other celluloses in the well-established characteristics (*a*) of reactivity with aniline—the rose-red colour reaction is sufficiently constant to be a measure of the proportion of esparto cellulose in admixture with cotton and wood celluloses, and (*b*) of yielding a constant high proportion of furfuraldehyde (12·5 per cent.) when decomposed with acids by the usual methods.

These are an index and measure of constitutional features of differentiation both of proximate and ultimate groups.

(2) Esparto cellulose is grouped with the cereal celluloses which present these same specific characteristics; but the latter are complex mixtures of structural elements, whereas esparto cellulose, as

paper-maker's "pulp," is a substantially homogeneous type—an assemblage of the fusiform, elongated cells which are identified as preponderating in the leaf structure by examination of transverse sections. It should be noted that the cereal celluloses are derived from stem tissues (straw), and the structural differentiation corresponds with difference of function.

(3) The cereal celluloses, as regards ultimate composition, are differentiated from the normal (cotton) celluloses by containing a lower percentage of carbon.

With Mr. Napper we have carefully purified specimens of esparto cellulose, and he has obtained the following analytical numbers with a specimen which, when dried at 100° in dry nitrogen, lost 'moisture' = 7·2 per cent., and on burning left 0·2 per cent. of ash:

0·1808 gave 0·2962 CO_2 and 0·0995 H_2O. C = 44·68; H = 6·16 per cent.*

These figures are approximately those required for the normal substance, and since the "furfuroid" constituent groups must be inferred from the yield of furfuraldehyde (12·5 per cent. as determined on the specimen in question) to be approximately 30 per cent. of the (esparto) cellulose aggregate, it would appear that the two component celluloses are identical in elementary composition. This does not allow any positive conclusions as to the generally assumed identity of 'furfuraldehyde-yielding' with pentosan groups. As, however, the full anhydride, of empirical formula $C_5H_8O_4$, requires C = 45·5 per cent., the evidence on this point, taken together with experimental facts set forth below, is rather against this assumption.

(4) It is noteworthy that as a result of the reaction with concentrated aqueous hydrochloric acid, as described in the foregoing paper, there is a loss of total furfuraldehyde, that is, a disappearance of "furfuroid" groups as such. This constitutional change has been studied and more definitely established by means of reactions calculated to determine the minimum of change in groups of normal hexose- or pentose-configuration.

These results are briefly as follows.

Action of Alkali Hydroxide.

(a) *Sodium Hydroxide* (*4 per cent.*) *at* 135°.—We must premise that esparto cellulose is isolated by digesting the raw esparto with 17 per cent. of its weight of 3—4 per cent. sodium hydroxide solution at 130° and under the corresponding pressure. It survives

* Calc. to (dry) ash-free substance.

this treatment with no change of furfuroid contents. Moreover, from the liquor we have isolated a colloidal or 'pectic' furfuroid, giving 50 per cent. of furfuraldehyde on boiling with hydrochloric acid. This is a higher yield than from any compound of this class hitherto obtained, and would appear to characterise it as a 'pure' pentosan. It is mentioned here only in reference to one point, namely, its behaviour with the hydrolysing acid employed in resolving the esparto cellulose (*infra*). The fuller study of this interesting substance is incidental to our scheme of research, which embodies the systematic fractionation and characterisation of these by-products of the industrial process, and the extension of our previous investigations (T., 1882, **41**, 94). The results of these researches will form the subject of future communications.

(b) *Sodium Hydroxide* (17·5 *per cent.*) *at* 15—20°.—Treatment with 'mercerising soda' is a standard method of diagnosing the proximate constitution of industrially important celluloses. The following numbers were obtained with the specimen in question, that is, the product from (*a*) subsequently purified by the usual basic bleaching process (bleaching powder):

α-Cellulose (resisting the solvent action)	84·14
β-Cellulose (soluble and reprecipitated on acidification)...	—
γ-Cellulose (hydrolysed : soluble in acidified liquid).....	15·86

[The specimen contained 1·3 per cent. of mineral constituents (ash), and the above figures are calculated on the ash-free cellulose.]

Action on Furfuroid Complex and Furfuroid Groups.

The yields of furfuraldehyde were:

Original cellulose. Per cent.	Cellulose after treatment.	
	α-Cellulose 84·14 : 4 per cent.	= 3·36
	γ-Cellulose 15·86 : 26 ,,	= 4·12
12·5	Total per cent.	7·48

There is an important constitutional change determined by the mercerisation: 40 per cent. of the ultimate furfuroid groups are affected, and the change of structure is more pronounced in the resistant (α) complex than in the hydrolysed groups (γ).

Action of Acids.

(a) *Acetylation.*—The cellulose was acetylated, with a yield of 160 per cent. of the weight taken. The acetate, by hydrolysis and condensation with hydrochloric acid, yielded 4·7 per cent. of furfur-

aldehyde, which, calculated on the original cellulose, is = 7·57 per cent.

There is a similar change of constitution in the furfuroid groups, and this notwithstanding the fact that acetylation under the conditions selected is ascertained to involve the minimum of structural change; in the case of the β-cellulose of jute it is without influence on the furfuroid groups ("Researches on Cellulose," I., p. 130).

(b) *Hydrolysing Acids.*—The cellulose was treated with five times its weight of sulphuric acid dihydrate, $H_2SO_4,2H_2O$.

(1) After three hours at 18° the viscous solution was diluted so as to correspond with a concentration of 1 per cent. of the original cellulose.

The figures for furfuraldehyde were as follows:

	Furfuraldehyde.	
	Per cent.	Percentage of original.
Reprecipitated fraction (colloidal hydrate) (23 per cent.)	4·6	1·06
Hydrolysed to soluble derivatives (77 per cent.)	8·6	6·62
Total		7·68

(2) In a second experiment, the whole of the resolved mixture was boiled with hydrochloric acid; an estimation of furfuraldehyde gave 7·5 per cent., calculated on the original cellulose.

(3) *Action of Sulphuric Acid Dihydrate on the Colloidal By-product (above).*—This concentrated form of furfuroid was similarly digested with the acid in the cold, and, after dilution, the solution was treated with hydrochloric acid as above, with the following result:

Furfuraldehyde	From original 50·0 per cent. After digestion 31·1 „

Here also we obtain the same result, 60 per cent. only of the furfuroid groups surviving as such.

The cellulose was next submitted to the action of sulphuric acid trihydrate, $H_2SO_4,3H_2O$.

(1) It was digested at 18° with five times its weight of the acid. The reaction is of a different order, as shown by the following results:

	Furfuraldehyde	
	Per cent.	Percentage of original.
Mixture of undissolved and reprecipitated (78·4 per cent.)	1·5	1·17
Hydrolysed to soluble forms (21·6 per cent.)	34·9	7·70
Total		8·87

(2) The experiment was repeated, using a larger proportion of the acid, which gave a more advanced resolution, as evidenced by the production of a homogeneous, viscous solution. On precipitation, 77·5 per cent. of the original was obtained in the colloidal hydrated form; the soluble hydrolysed products also yielded, as before, 35 per cent. of furfuraldehyde.

(3) The effect of prolonging the digestion for six days at 15—18° was next examined, with the following results:

	Furfuraldehyde	
	Per cent.	Percentage of original.
Reprecipitated hydrated colloid (61 per cent.) ...	1·1	0·67
Hydrolysed to soluble derivatives (39 per cent.)	19·9	7·76
Total		8·43

It is clearly established by this study of the furfuroid groups of esparto, both of the cellulose and non-cellulose components, that they are in a labile and potentially transitional form, and further doubt is cast on the very usual assumption that these furfuraldehyde-yielding carbohydrates are pentosans. These results must also be reviewed in the light of the data of the foregoing paper by Miss Cunningham.

The variations of the primary factors of reaction, cellulose, as well as acids, were carefully designed to extend the basis of criticism; there are many directly consequent results, and conclusions which require no further discussion. *The main result is to restore the cellulose–dextrose relationship to the position of an open question and problem.* It is now once more and more positively emphasised that the supposed proofs of a lineal descent are of doubtful validity. It should be recognised that the intervening factor of the unexplored colloidal state is very seriously to be reckoned with, not only on an a priori criticism of the assumed constitution of cellulose as a complex of actual hexosan (or hexose–pentosan) groups, but for its evident influence on the whole of the reactions described in this and the foregoing paper.

Thus we have to account for the fixation of SO_4H (or SO_4) in stable union by reaction with sulphuric acid dihydrate; no such reaction would appear to be possible with a hexose or even with an anhydride. Rather as a matter of form, we have examined the behaviour of dextrose with these acids. There is no fixation of SO_4H and no development of acid function by any constituent hydroxyl group.

As regards the possibility of a reaction between sulphuric acid and an alcoholic hydroxyl group, there must be simultaneous resolution of the sulphuric acid dihydrate, which implies a considerable (endo) thermal effect. It is therefore necessary to make a thermal

study of the reaction, and this will be undertaken with other typical cases which are already under investigation.

The simplest interpretation of the reaction in the meantime is that the effect is initiated with groups of *the complex* containing oxygen of basic function in excess of that which characterises any hexose or hexose anhydride. A nucleus group of this order may very well derive its basicity from a special configuration due to the affinity strains of the colloidal system. That such exist and are brought into play by reactions of this order is shown by the changes produced in the furfuroid groups of the esparto cellulose by reactions of a by no means energetic character, and in the case of the normal celluloses by the changes which we have specially investigated in our study of the reaction with formic acid (T., 1911, **99**, 1450).

It is still undetermined whether the product is a true ester or an ester hydrate, the latter being the analogue of the salts formed by the interaction of the colloidal hydroxides of the metals and the acid in aqueous solutions. It is also undetermined whether the acidity of the derivatives in excess of that due to SO_4H is the result of migration of hydroxyl groups attending the reaction or a secondary effect due to the entrance of SO_4 residues into the complex. That the former is probable is shown in the results obtained by Ost and Wilkening (*Chem. Zeit.*, 1910, **34**, 461) in their endeavour to prove the total hydrolysis of cellulose to dextrose. There was an invariable production of acids of low molecular weight (volatile acids) in many cases in considerable proportions.

Since the researches of which this and the foregoing paper are sections are in progress, we limit ourselves to experimental records and a brief treatment of the theoretical points which are present difficulties, but also a definite forecast of lines of progress.

As our present main subject is esparto cellulose, we may perhaps be allowed to direct attention to the change of paper used in printing this Journal—as from January, 1918—from the esparto cellulose type to a paper composed of wood and cotton celluloses.

A main reason for this change is the special reactivity of esparto cellulose with arylamines and derivatives, as described above. Those directly responsible for the publication of the Journal have been in difficulties as regards paper supplies, and it was deemed opportune to take advantage of the position by considering the technical problems involved and adopting a standardised paper, free from the particular defect in question.

3 & 4 New Court,
Lincoln's Inn
London.

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XXIII.—*The Constitution of the Disaccharides. Part II. Lactose and Melibiose.*

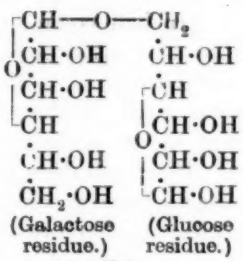
By Walter Norman Haworth and Grace Cumming Leitch.

Our present knowledge of the structure of the disaccharides is mainly restricted to the elementary facts that these sugars yield hydrolytic products which may be recognised and classified as one or other of the simple monosaccharides. Although many constitutional formulæ have been proposed for lactose, experimental work leading to the solution of this important problem has hitherto been lacking. Fischer's suggestion (*Ber.*, 1888, **21**, 2633) of the acetal type of linking of the two constituent hexoses cannot now be upheld, and the steady adherence of chemists within recent years to the γ-oxidic mode of representation of the hexoses further excludes formulæ based on the conception of these sugars as aldehydes (Fischer, *Ber.*, 1893, **26**, 2400; 1894, **27**, 2988).

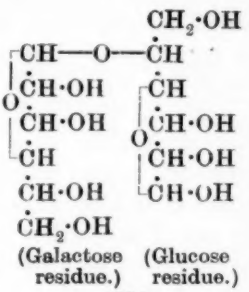
That lactose is an anhydride of the two so-called aldo-hexoses, glucose and galactose, has long been known, and, inasmuch as it is also a reducing sugar, the active terminal group of one of the hexoses must necessarily be preserved in the structure of the disaccharide. Evidence is adduced on p. 192 showing that the reducing property which persists in lactose is attributable to the glucose residue, and that the similar property of the galactose residue has become latent by its combination with the glucose molecule. This mode of linking of the two hexoses, engaging as it does the reducing group of galactose, must therefore occur by combination of the latter with one of the hydroxyl groups of the glucose chain, and the allocation of the precise form and position of the linking constitutes the outstanding difficulty in assigning a definite formula to the disaccharide.

An important contribution to the study of lactose has been made by Ruff and Ollendorff (*Ber.*, 1900, **33**, 1802), and their conclusions are discussed in greater detail on p. 192 of this communication. Their researches have shown that the anhydride-linking of galactose with glucose does not concern the hydroxyl groups attached to the second and third carbon atoms from the reducing end of the glucose chain. If we are also to exclude the hydroxyl position next in order, on the ground of its being occupied already in the γ-oxide linking of the glucose structure, which is definitely known to be the case (p. 193), then there remain open to us two alternatives, namely, that the galactose-reducing group, in its union with the glucose, involves either the hydroxyl group attached to

the terminal carbon atom of the chain, or the adjacent penultimate hydroxyl group:



(I.)



(II.)

One or other of these formulæ must therefore represent both lactose and its synthetic stereochemical isomeride, *iso*lactose, and the final allocation of one of them to lactose and *iso*lactose leads to the inference that the alternative formula should be ascribed to melibiose, the disaccharide obtained by the partial hydrolysis of raffinose. We are now able to advance conclusive evidence in favour of the adoption of the second of these formulæ for lactose. Consequently, it follows that, according to our present knowledge of the chemistry of melibiose, formula (I) best represents the latter sugar. The possibility, however, that the hydroxyl group attached to the third carbon atom of the glucose residue is concerned in the linking with galactose in the melibiose molecule is not altogether excluded by the evidence available. In the case of lactose, no such dubiety remains.

This conclusion is of peculiar interest, apart from its relation to the solution of the immediate problem of the structure of lactose, in that it offers definite evidence of the hitherto unknown mode of linking of two sugar molecules in the form of a branched chain,

$$>CH\cdot O\cdot CH<\begin{matrix}CH_2\cdot OH\\ CH(OH)\end{matrix}.$$

as shown in the lactose formula (II). Without some such hypothesis, it has always been a matter of difficulty to account for the numerous isomerides existing in the disaccharide series, and there can no longer be any reluctance in offering as an explanation of the occurrence of these isomerides the supposition that the reducing group of one hexose is united with a second residue through any one of the hydroxyl groups of the latter. Thus there are no fewer than four reducing disaccharides containing two glucose residues, namely, maltose, *iso*maltose, gentiobiose, and cellobiose, and the existence of these is explicable on the above grounds.

As an initial step in the investigation of the constitution of

lactose, experiments were instituted on the methylation of this sugar by the agency of methyl sulphate as alkylating medium, and a detailed description of the general applicability of this reagent in the sugar group has been given in a previous communication (Haworth, T., 1915, **107**, 8). The utility of methyl iodide and silver oxide for the methylation of sugars is confined to the non-reducing derivatives, such as the glucosides, since, in the presence of a reducing sugar, silver oxide functions as an oxidising agent, and esters of carboxylic acids are formed. This limitation imposed on the use of the earlier reagent has hitherto been an obstacle to the investigation of methylated disaccharides, inasmuch as the preparation of the methylglucosides of bioses is attended with considerable difficulty. Thus, as initial materials for an extended investigation, they are comparatively inaccessible.

With the view of determining the best experimental conditions for the direct methylation of reducing sugars, glucose was selected as an example. Methylation of the reducing group of the sugar proceeded by the aid of methyl sulphate and sodium hydroxide at a moderately low temperature, and methylation of all the hydroxyl positions was completed at a higher temperature. The crystalline product isolated in good yield was tetramethyl β-methylglucoside (see p. 195). Since this substance may be hydrolysed with greater ease than the α-modification, the present procedure is recommended as the best method of preparing tetramethyl glucose in quantity.

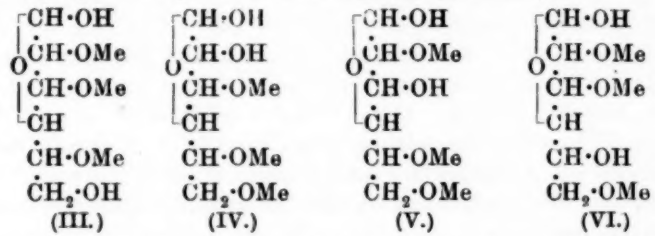
Conditions having now been established in the case of glucose, these were applied to the direct methylation of lactose, with satisfactory results. The eight hydroxyl positions in the disaccharide molecule were found to have been completely methylated, and heptamethyl methyllactoside was obtained in minute, colourless crystals melting at 77—82°, and showing a rotation of $[\alpha]_D$ +5·2° in water and −16·9° in ethyl alcohol. This crystalline variety, on the analogy of the glucose experiment, was probably the β-modification, and what is conceivably the α-form was also isolated as a colourless oil distilling at 210°/1·1 mm. Simultaneously, a quantity of hexamethyl methyllactoside was also prepared.

A portion of the heptamethyl methyllactoside was submitted to hydrolysis with 5 per cent. aqueous hydrochloric acid at 80°, and finally in the region of 100° for a brief period. Practically no hydrolytic cleavage occurred at a lower temperature than 80°. From the syrupy product two methylated hexoses were isolated, one of these being tetramethyl galactose, which was identified by conversion into the crystalline anilide melting at 192°, and showing the equilibrium value $[\alpha]_D$ +38·0° after catalysis. These data agree with those of the anilide of tetramethyl galactose prepared

by Irvine and McNicoll (T., 1910, **97**, 1454), and, moreover, a mixed melting-point determination proved the identity of the present specimen, derived from methylated lactose, with a specimen provided by the above authors.

Complete separation of the methylated galactose fragment having been effected through conversion into the anilide, the remaining syrup, on keeping in a desiccator, crystallised in minute needles. The latter compound, melting at 118—119°, was shown to be a trimethyl hexose and represented the glucose fragment from the hydrolysis of the lactoside. Its stability towards permanganate indicated that it belonged to the butylene oxide type of sugars. Since eight methoxyl groups were originally present in the heptamethyl methyllactoside, and four of the methoxyl groups have been acounted for by the isolation of the tetramethyl galactose fragment, whilst one methoxyl group was removed as the glucosidic group, there remain only three other methoxyl groups to be allocated. These could only have been present in the glucose fragment, and thus the isolation of the trimethyl hexose establishes its identity as a trimethyl glucose.

There are possible only four trimethyl glucoses of the butylene oxide type possessing a free reducing group, namely:



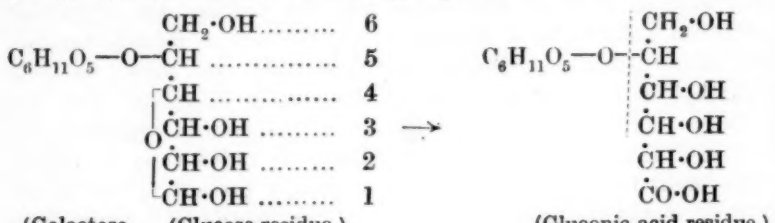
(III.) (IV.) (V.) (VI.)

The trimethyl glucose isolated in the present case does not form an osazone, and thus formula IV is excluded on these grounds. Again, the trimethyl glucose of formula III is known, and this is a liquid having a different rotation from that of the substance now isolated (Purdie and Bridgett, T., 1903, **83**, 1039).* The choice of a formula for the crystalline trimethyl glucose obtained from heptamethyl methyllactoside is thus restricted to formulæ V and VI. Fortunately, by having regard to the behaviour of lactose itself, we are able to decide between these two alternatives. Lactose gives rise to a phenylosazone, and also may be made to undergo oxidation with bromine water to lactobionic acid (VIII). By hydrolysis of the latter, Fischer and Meyer obtained gluconic acid and galactose (*Ber.*, 1889, **22**, 361), and from the former

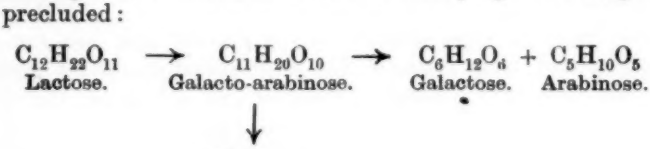
* The constitution originally assigned to this liquid trimethyl glucose has recently been confirmed by Irvine and Dick (unpublished research).

glucosone and galactose were isolated as cleavage products (Fischer, *Ber.*, 1888, **21**, 2633).

From these facts, it is clear, first, that in lactose the reducing group of the glucose residue is free; secondly, that the hydroxyl group adjacent to this reducing group is also free:



Again, Ruff and Ollendorff (*loc. cit.*) were able to degrade lactose to the galacto–arabinose by oxidising the calcium salt of lactobionic acid with Fenton's reagent. The syrupy sugar was found to yield on hydrolysis *d*-galactose and *d*-arabinose, and therefore was a hexose–pentose complex, isomeric with vicianose. This compound readily formed a phenylosazone, and therefore the hydroxyl group adjacent to the reducing group of the arabinose residue must be free; hence it is proved that two of the secondary alcohol groups which are situated nearest to the reducing group in the original lactose molecule must be free, that is, the hydroxyl groups attached to the carbon atoms numbered 2 and 3 in formula VII, since the carbon atom marked 1 is eliminated by the process of degradation. The consideration of formula V as representing the constitution of the trimethyl glucose fragment is thus precluded:



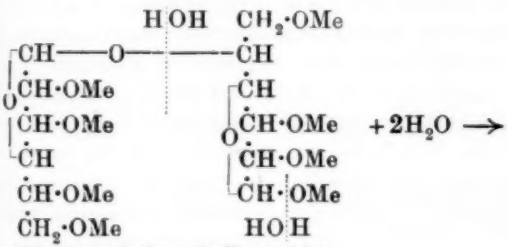
This result leaves open only three possible positions for the coupling of the galactose residue with glucose in the lactose molecule, namely, the secondary alcohol groups attached to the fourth and fifth carbon atoms and the terminal primary alcohol group of the glucose chain (see formula VII, above).

In the course of the present investigation it has been shown

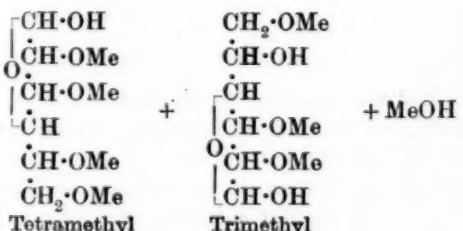
* In elucidating these transformations the structural formula for lactose determined in the course of the present communication is used throughout. In order to simplify reference, numbers are ascribed to the different positions in the sugar chain.

that the trimethyl glucose fragment, obtained on hydrolysis of heptamethyl methyllactoside, is of the butylene oxide type, and thus the secondary alcohol group of the fourth carbon atom of the glucose chain is occupied by this butylene oxide linking. Further, as already stated (p. 191), evidence is available that this trimethyl glucose cannot be represented by formula III, and thus the primary alcohol group cannot have been concerned in the galactose coupling. As formulæ IV and V given above are also excluded by experimental evidence, there remains, then, the only other possibility, namely, that the trimethyl glucose isolated from the hydrolysis of heptamethyl methyllactoside has the constitution represented by formula VI.

Since this is so, it follows that the constitution of lactose is also clearly indicated: in the disaccharide the galactose residue is combined through its reducing group with the glucose residue, and involves in this union the secondary alcohol group attached to the fifth carbon atom of the glucose chain, for the latter grouping remains unprotected by a methyl group in the trimethyl glucose isolated, and must consequently have been concerned in the disaccharide linking in the completely methylated lactose. The hydrolysis of heptamethyl methyllactoside may thus be formulated as below, the dotted lines indicating the points of cleavage:



(Heptamethyl methyllactoside)
(IX).

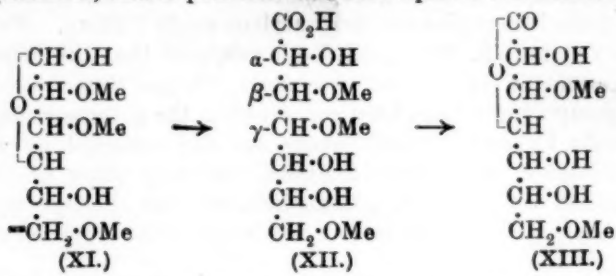


Tetramethyl galactose. (X.)

Trimethyl glucose. (VI.)

A trimethyl glucose, identical with that obtained from lactose in the course of this work, was also isolated by Denham and Wood-

house from methylated cellulose (see p. 199). This has the same crystalline form, its melting point is not depressed by mixing the two specimens, and it possesses the same equilibrium rotation value.



(XI.) (XII.) (XIII.)

These workers prepared from it the trimethyl heptonic acid (XII) by ascending the series, and showed that this acid only undergoes lactone-formation at the expense of the loss of a methyl group (XIII). The methyl group eliminated by the lactonisation was considered by the authors to be that having the γ-position, and the constitution they tentatively ascribed to the trimethyl glucose is represented by formula XI, which is identical with formula VI (p. 191).

We are thus able to confirm the structure assigned to this trimethyl glucose, and it is of interest that the same mode of dihexose linking that occurs in cellulose is also present in lactose.

Since lactose is hydrolysed by lactase, which is the specific enzyme for β-galactosides, just as emulsin is the enzyme for β-glucosides, therefore the two known forms of α- and β-lactose are to be regarded as the α- and β-glucose-β-galactosides. Presumably the synthetic *iso*lactose, concerning which little is known chemically, is the stereoisomeric glucose-α-galactoside, whilst melibiose may be considered to be the structurally isomeric glucose-β-galactoside possessing the constitution I (p. 189).

Experimental.

Preparation of Tetramethyl β-Methylglucoside.

For the purpose of this preparation, 27 grams of glucose were dissolved in 10 c.c. of water. There were also required 142 grams of methyl sulphate (109 c.c.) and a solution containing 109 grams of sodium hydroxide in 190 c.c. of water. One-fifth of the above volume of methyl sulphate was added immediately to the glucose solution, and the temperature of the mixture maintained at 35° by surrounding the vessel with warm water. From a dropping funnel, 38 c.c. of the sodium hydroxide solution were introduced slowly, drop by drop, with efficient mechanical stirring. There-

after the temperature was raised to 40°, and then, gradually, over a period of three hours to 60°.

By this time the glucose was almost completely converted into β-methylglucoside. The temperature was now maintained at 60° while the remainder of the sodium hydroxide solution and methyl sulphate was slowly added in approximately equivalent amounts in unit time from two dropping funnels, the mixture being meanwhile vigorously stirred.

When the whole of the reagents had been added, the temperature was raised to 100°, and, after keeping for half an hour at this temperature the reaction was complete. On cooling, the aqueous solution was extracted with chloroform, the extract dried, and the product distilled. Almost the whole of the residue remaining after the removal of the solvent distilled at 108—110°/0·23 mm. as a colourless oil having n_D 1·4455. Other fractions distilling up to 150° were small in amount and had refractive indices varying from 1·4495 to 1·4708, and these consisted of partly methylated glucosides. The first fraction crystallised instantly on nucleation with a crystal of tetramethyl β-methylglucoside, which had previously been prepared by Purdie and Irvine (T., 1904, **85**, 1064), and the crystals, after draining on porous tile, melted at 39—41°. A mixed melting-point determination with the specimen previously prepared by the older method showed no depression. The rotation of the substance in absolute ethyl alcohol was $[\alpha]_D$ −13·3° (c=5·0). The following analytical data were determined:

0·1347 gave 0·6125 AgI. OMe=60·03.

$C_6H_7O(OMe)_5$ requires OMe=62·0 per cent.

The Complete Methylation of Lactose.

Isolation of Hexamethyl Methyllactoside and Heptamethyl Methyllactoside.

A convenient method of conducting the methylation of a disaccharide may be illustrated by the use of lactose. The materials were used in the following proportions: lactose (30 grams), methyl sulphate (114 c.c.), sodium hydroxide (111 grams), dissolved in water (210 c.c.). The lactose was dissolved in the minimum amount of hot water and the solution cooled to 30°. One-eighth of the above volume of methyl sulphate was added, followed by one-eighth of the total volume of the sodium hydroxide solution. The latter reagent was added very slowly with mechanical stirring, and the temperature of the mixture maintained at 30° by means of a water-bath.

This treatment was repeated, one-eighth of the original volume

of methyl sulphate being mixed with the lactose solution, and again one-eighth of the sodium hydroxide solution slowly introduced, while the temperature was maintained at 40°.

The mixture was kept overnight, and on the following day the reducing property of the free sugar was found to have disappeared. It is important that throughout all these operations no free alkalinity should be allowed to develop, otherwise scission of the disaccharide occurs. Thereafter the temperature was raised to 60°, and a third proportion corresponding with one-eighth of the original volume of methyl sulphate was introduced, and a similar proportion of sodium hydroxide solution was added, drop by drop, with vigorous stirring. The remainder of the reagents was added at 70° in the same order and in similar fractions, stirring being continued throughout the addition. Finally, the temperature was raised to 100° for a period of half an hour, when the reaction seemed to be complete. Extraction of the product was carried out with chloroform, the extract dried, and the solvent distilled. A residue was obtained which yielded four fractions on distillation:

I.	160–193°/0·2 mm.	
II.	193°/0·22 mm.	n_D 1·4759.
III.	204–210°/0·38 mm.	n_D 1·4760.
IV.	217°/0·63 mm.	

The third fraction, on analysis, gave results agreeing with the formula of hexamethyl methyllactoside:

0·1955 gave 0·7190 AgI. OMe = 48·55.

$C_{12}H_{15}O_4(OMe)_7$ requires OMe = 49·32 per cent.

0·1308 gave 0·2450 CO_2 and 0·0969 H_2O. C = 51·1; H = 8·23.

$C_{19}H_{36}O_{11}$ requires C = 51·8; H = 8·20 per cent.

A determination of the optical activity of this fraction in water gave $[\alpha]_D$ +7·47° (c = 4·28), and this value shows a considerable diminution in the specific rotation of the original lactose ($[\alpha]_D$ +52·2°).

When the material represented by the fractions I—IV was twice further methylated, either with methyl sulphate and sodium hydroxide, or, alternatively, with silver oxide and methyl iodide, it was found that the bulk of the product consisted of heptamethyl methyllactoside, as shown below. This was submitted to distillation under diminished pressure by means of the Gaede pump.

Fraction I.	185°/0·05 mm.	n_D 1·4559.
Fraction II.	195°/0·05 mm.	n_D 1·4688.
Fraction III.	200°/0·05 mm.	n_D 1·4713.

Fractions I and III were exceedingly small in amount.

The main fraction gave the following analytical data:

0·0586 gave 0·2368 AgI. OMe = 53·34.
$C_{12}H_{14}O_3(OMe)_8$ requires OMe = 54·63 per cent.

0·1352 gave 0·2585 CO_2 and 0·1025 H_2O. C = 52·16; H = 8·43.
$C_{20}H_{38}O_{11}$ requires C = 52·83; H = 8·43 per cent.

It was observed that this major fraction (II) crystallised on keeping, and especially on triturating with light petroleum. The crystals were drained on porous porcelain and recrystallised from light petroleum.

The colourless needles melted at 77—82°, and a determination of the refractive index of the superfused solid gave n_D 1·4675.

Complete analytical data were now obtained for the crystalline specimen:

0·1002 gave 0·4175 AgI. OMe = 55·0.
$C_{12}H_{14}O_3(OMe)_8$ requires OMe = 54·63 per cent.

0·1281 gave 0·2482 CO_2 and 0·0974 H_2O. C = 52·84; H = 8·44.
$C_{20}H_{38}O_{11}$ requires C = 52·83; H = 8·43 per cent.

and the rotation of this pure specimen of heptamethyl methyllactoside was determined in different solvents:

Rotations: I. Water $[\alpha]_D$ +5·19°; c = 0·771.
II. Absolute ethyl alcohol −16·87°; c = 1·482.
III. Methyl alcohol −13·04°; c = 1·459.
IV. Acetone −13·64°; c = 1·1466.

Hydrolysis of Heptamethyl Methyllactoside.

Preliminary experiments on the hydrolytic cleavage of this completely methylated lactoside showed that the hydrolysis occurred probably in two stages. With 5 per cent. aqueous hydrochloric acid, after two and a-half hours' heating at 80°, scission of the disaccharide linking takes place, and the specific rotation at this point is of the order of $[\alpha]_D$ +66°. Prolonged heating at this temperature, or a short period of heating at 98°, results in the removal of the methylglucoside linking, and the specific rotation registered is about $[\alpha]_D$ +76°. A larger quantity of material was then subjected to similar treatment, and the product, consisting of a mixture of methylated hexoses, was separated into its individual components in the following way. The aqueous hydrochloric acid solution was neutralised with barium carbonate and evaporated to small bulk in a vacuum. The syrupy residue was extracted with ether to remove mineral salts, and, after filtration from these, the ethereal solution was evaporated. It was anticipated that the methylated hexoses derived from this hydrolysis would be (1) a tetramethyl galactose, (2) a trimethyl glucose. The former of

these may be expected to possess solubilities differing from those of the latter, owing to its containing fewer free hydroxyl groups. Ultimately it was seen that a separation of the methylated galactose and glucose fragments could be effected by taking advantage of the insolubility of the anilide of tetramethyl galactose in water, the anilide of the other methylated hexose present being soluble. The dried, syrupy residue above mentioned was therefore digested with an alcoholic solution containing excess of aniline (7 molecular proportions) for three hours. On cooling, colourless crystals of an anilide separated. The whole of the mixture was subjected to steam distillation in order to remove the excess of aniline, and from the undistilled residue there separated crystals of crude anilide. Thus, in one experiment, from 2·55 grams of hydrolysed syrup 1·2 grams of crystalline anilide were obtained. This was filtered and recrystallised from ethyl acetate, when long, silky, colourless needles, which matted together on filtration, were obtained melting at 192° without decomposition. Polarimetric examination of the anilide in acetone solution gave $[\alpha]_D$ +38·0° as the equilibrium value after catalysis. These data agree with those of the anilide of tetramethyl galactose prepared by Irvine and McNicoll (T., 1910, **97**, 1454).

A mixture of the above anilide with a specimen prepared by the latter authors showed no depression in melting point, and thus there can be no doubt of their identity.

On another occasion a highly purified specimen of the anilide was isolated in this way from the products of hydrolysis, and more accurate optical data were obtainable. These may now be given as $[\alpha]_D$, initial value −83·3°, falling to the permanent equilibrium value $[\alpha]_D$ +40·7°.

The filtrate from the crystalline anilide contained in solution another anilide, presumably that of the methylated glucose fragment. The addition of a trace of mineral acid caused the separation of aniline, which was removed by distillation in a current of steam, and the residual solution was concentrated in a vacuum at 20°. A moist syrup remained behind which weighed 1·3 grams; this was dried by solution in absolute alcohol, the solvent distilled, and from the residual syrup there separated minute needles which, after recrystallisation from dry ether, melted at 118—119°. The sparing solubility in dry ether of this colourless substance, its stability towards permanganate, and its melting point indicated that it was probably identical with the trimethyl glucose obtained by Denham and Woodhouse from methylated cellulose (T., 1914, **105**, 2364; 1917, **111**, 244). Confirmation on this point was forthcoming, as for the purpose of comparison we were able, by

the courtesy of these authors, to obtain a specimen of the trimethyl glucose prepared by them. This specimen, which had been kept for some months, was found to melt at 114°, but after recrystallisation it melted at 117°. The solubilities, crystalline form, and melting point of this recrystallised specimen, and also a mixed melting-point determination (117—118°), proved the identity of the two specimens, so that there can be no doubt that the colourless, crystalline substance obtained as the second cleavage product of heptamethyl methyllactoside is a trimethyl glucose.

The initial value for the specific rotation in methyl alcohol was determined, namely, $[\alpha]_D$ +112·9°; after catalysis with a trace of hydrochloric acid, the reading diminished to an equilibrium value $[\alpha]_D$ +69·1°. It will be seen that the initial rotation recorded is slightly higher than the value ($[\alpha]_D$ +103·9°) quoted by Denham and Woodhouse (*loc. cit.*), whilst the equilibrium value is almost identical with that quoted by them for an acetone solution of the substance (69·5°). This slight variation in the magnitude of the initial rotation may be explicable on the ground that the melting point found by ourselves is 8° higher than that quoted by the former authors in their communication, so that from methylated lactose the compound may be more readily obtainable as a pure stereochemical form. The crystalline compound combines with phenylhydrazine in the cold, giving an oily phenylhydrazone, but no phenylosazone derivative could be prepared.

We can also confirm the constitution assigned to this compound, and a discussion of the formula (VI) is included in the theoretical part of this communication.

We acknowledge our indebtedness to the Carnegie Trust for a scholarship which has enabled one of the authors to collaborate in this investigation.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

[*Received, February* 28th, 1918.]

Recent Studies on Active Nitrogen.

A Lecture delivered before the Chemical Society on February 21st, 1918.

By the Hon. Robert John Strutt.

In 1913 I gave a Friday evening lecture at the Royal Institution, in which some of the more striking phenomena of active nitrogen were exhibited. This evening I shall dwell chiefly on results obtained since that time, but to be intelligible to those coming fresh to the subject, it will be necessary to traverse a little of the old ground.

The fundamental experiment on this subject is to pass a stream of rarefied nitrogen through a discharge tube *a* (Fig. 1) in which a vigorous jar discharge is maintained. The stream of gas, drawn by a powerful air pump, issues into the vessel *b*, where it exhibits a brilliant yellow light. The fact that no electric discharge passes in *b* and that the gas takes an appreciable time to pass through this vessel shows that it remains glowing after the electric discharge is over, and this may be established very directly by simply turning the exciting discharge off, when the luminosity will be seen to persist for some seconds' interval flowing down into the pump. Indeed, in favourable circumstances and with a closed vessel scrupulously clean, the luminosity persists for several minutes.

Evidently this luminosity (which is not of the nature of temperature-radiation) can only be maintained by the passage of the nitrogen gas from a state in which it contains more potential energy to a state in which it contains less. This circumstance alone might suggest that a special modification of nitrogen is present, but this becomes a certainty when we note the behaviour of the glowing gas when other gaseous substances are brought in contact with it. For it is found that hydrocarbons are converted at the ordinary temperature into hydrocyanic acid, and that the more volatile metallic vapours are converted into nitrides.

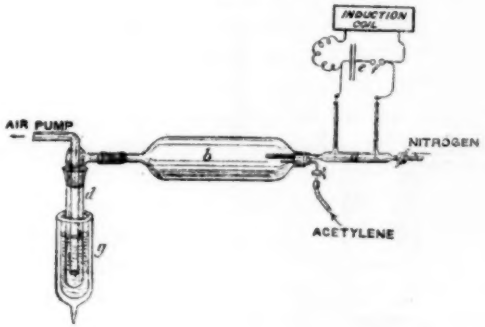
Ordinary nitrogen will certainly not behave in this way, and therefore it does not seem over-bold to assume that an extraordinary kind of nitrogen is present. This has been named, with a minimum of hypothesis, active nitrogen. So far as I am aware, no alternative interpretation of the facts mentioned has been attempted.

In some of the developments of radioactivity, it has been an unfortunate necessity to work with quantities so small that often

they could not be weighed or even seen. It may be remarked in passing that whatever legitimate scepticism may have been felt about results so attained, at any rate they have led to conclusions which can be verified by the well-tried methods of the chemical analyst. It suffices to refer to the now established fact that there are various kinds of lead of different atomic weights.

There is, or has been, an idea abroad that my conclusions on active nitrogen are dependent on similar indirect methods: that the evidence for the existence of an active modification of nitrogen depends on a dubious interpretation of obscure spectroscopic phenomena. I hope this evening to make it quite clear that this is not the case. In fact, I should not have had the courage to face you to-night if I had not had more direct and convincing evidence to offer. I wish to emphasise that the existence of active nitrogen was formulated solely on the grounds which appeal most directly

FIG 1.



to chemists. The properties of this substance have been examined by the ordinary methods of chemical analysis, carried out in many cases, not on a microscopic scale, but in vessels of ordinary or even large size, dense precipitates and strong colorations being obtained such as do not require the eye of faith for their recognition.

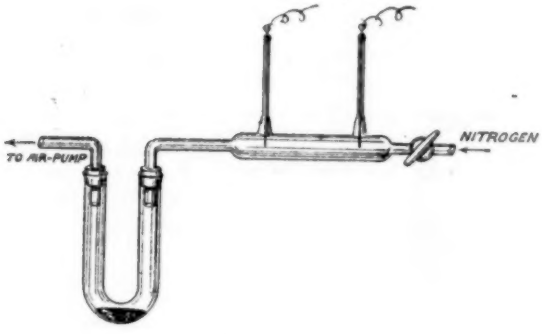
Although the luminous phenomena accompanying these actions form no part of the evidence for the existence of the active substance, yet they are of considerable interest in connexion with its properties, and I shall have a good deal to say about them.

I first show you the action of active nitrogen on acetylene. When acetylene enters the stream of yellow, glowing gas, you see that a lilac tint is developed. This shows the well-known cyanogen spectrum—the spectrum obtained, for instance, from burning cyanogen; and it was for this reason that it was first suspected that hydrocyanic acid was formed. It would, however, be most

unsatisfactory to rely on such an argument. I do not, and never did rely on it. In showing the presence of hydrocyanic acid, I have generally frozen it out from the gas stream with liquid air (as in Fig. 1) and shown its presence chemically in the cooled vessel *d*. To-night, however, a simpler method must suffice. We lead the gas ejected by the pump through a solution of sodium hydroxide to collect the hydrocyanic acid. On adding a mixture of ferrous and ferric salts, and acidifying, you see that a strong Prussian-blue reaction is obtained.

I have shown on previous occasions the action of active nitrogen on mercury vapour. Mercury was gently heated in a stream of the yellow, glowing gas, and it was found that the yellow glow was displaced by the green light of mercury, familiar in the mercury vapour lamp, with its characteristic line spectrum. At the same time, a nitride is produced. This may be treated with water, when

FIG. 2.



ammonia is formed, and the Nessler reaction is obtained. The nitride is unstable, and when heated pretty strongly it decomposes with minute flashes, accompanied by audible crackling.

I shall now perform a novel experiment, not before shown publicly. This is the action of active nitrogen on cold liquid mercury. The stream of glowing gas is led over a U-tube (Fig. 2) containing a small quantity of clean mercury, not enough to fill the bottom bend of the tube. So long as the tube is at rest nothing happens, the glowing gas passing on; but if the tube is shaken so as to break the skin of the mercury surface, and constantly to renew it, it is seen that the mercury is quickly attacked and becomes foul, very much after the fashion in which it is made foul by ozone. At the same time, the luminosity of the issuing gas is extinguished, showing that it is no longer in the peculiar state.

Let us now take some of the mercury which has been made foul

in this way, mix it with water, distil off a portion, and test with Nessler's solution. You will have no difficulty in recognising the presence of ammonia, showing that a nitride had been formed.

One interesting point is that when liquid mercury is employed in this way we do not get any trace of the mercury spectrum, so conspicuous when active nitrogen mingles with mercury vapour, but the chemical reaction occurs none the less. Thus it appears that we cannot trace any close or necessary connexion between the luminous effects and the chemical ones.

I will now direct your attention to another interesting case of this kind. Suppose that nitrogen is purified by allowing it to remain over cold phosphorus, and then thoroughly dried by passage through long and tightly packed tubes filled with phosphoric oxide. In these circumstances, it will be tolerably free from traces of oxygen compounds, and the afterglow of the gas, usually yellow, will be found to be practically invisible through a blue glass. Suppose now that we allow a small quantity of almost any oxygen-containing gas to flow into the stream of glowing nitrogen, taking care, however, to prevent it from mixing with the nitrogen until the latter has left the discharge. Nothing particular seems to happen when the oxygen compound flows in, so long as we observe the yellow light directly, except that the yellow light fades out sooner; but if a blue glass is interposed to cut out the yellow light, then we see that at the confluence a bluish-violet light is developed by admixture of the gases. This bluish-violet light is to a great extent masked by the yellow when no colour-filter is used.

The same thing can be recorded photographically, using first an isochromatic plate with yellow screen, then an ordinary plate with a blue screen.*

Oxygen itself, or carbon monoxide or dioxide, or nitrous or nitric oxides, will give this effect when introduced into the yellow-glowing gas. I wish you particularly to notice that in these experiments the admixture does not get back to the discharge tube. It never comes in contact with the electric discharge at all. Only nitrogen goes through the discharge. The oxygen-containing gas is mixed with it afterwards.

The yellow light when spectroscopically analysed shows a selection of the bands produced by nitrogen in a vacuum discharge, although omitting many of them in a very strange way. It is simply a nitrogen spectrum. But what of the bluish-violet light? Although I have spoken of it as bluish-violet, it is really in the main ultra-violet, and it consists of two sets of bands, which have

* Or no screen at all, for the photographic action of the yellow light in the latter case is relatively too weak to be worth considering.

been called, for the sake of distinction, the β- and γ-groups of bands. The β-bands are not at present known to be produced in any other way, but the γ-bands occur when oxides of nitrogen (nitrous or nitric) are introduced into a Bunsen flame. They do not occur in a Bunsen flame burning in the ordinary way, which, of course, contains oxygen and nitrogen separately, and these facts, taken together, would seem to suggest very distinctly that the spectrum in question indicates oxidation of nitrogen. Is there, then, any oxidation when oxygen is led into active nitrogen, and this spectrum results? Careful tests of the products with the extremely sensitive tests available (Griess's reagent) have convinced me that no oxides of nitrogen are produced. I have been reluctant to accept this conclusion, and have returned again and again to the subject, always with the same result. It would have been satisfactory to find that the isolation of active nitrogen would help us to understand the processes occurring in the arc process for oxidising nitrogen, and it is still possible that something of the kind may be made out. Koenig and Elöd in Germany have stated that a particular kind of active oxygen (not ozone) can be produced by electric discharge which will unite directly with active nitrogen. I have attempted to repeat these experiments, but have hitherto been unable to satisfy myself of their correctness. I do not wish, however, to speak too positively on the subject.

However this may be, it is remarkable that whilst active nitrogen will attack carbon compounds, even methane, to form hydrocyanic acid, it will not react either with oxygen or with hydrogen.

Hitherto, we have considered chiefly the properties of active nitrogen when formed. It is also of interest to consider the conditions for its formation. These present many puzzling problems, and in this connexion I shall have to content myself chiefly with recording facts rather than theories.

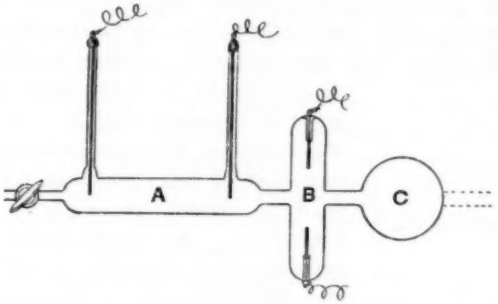
Let us first consider what kind of electrical conditions are best. In the first place, it is far preferable to work at a low gaseous pressure, a few mm. of mercury. The reason for this seems to be that collision with ordinary nitrogen molecules tends in some way to the destruction of active nitrogen, although how this occurs is not clear.

The next point is that a Leyden jar discharge is much preferable to the discharge of an induction coil without a jar. As is well known, the effect of the jar is to store up electricity and allow it to discharge suddenly through the gas. In these circumstances, the momentary current density is very high, and the nature of the discharge is altered in other respects: the peculiar phenomena of negative dark space and negative glow are obliterated, and the

spectrum of the light along the length of the discharge is modified, losing its reddish colour and becoming much bluer. At the same time, the production of active nitrogen is much increased. Accordingly, the jar discharge is generally used in experiments on active nitrogen.

Not only is the jar discharge the best, but if an uncondensed discharge (without jar) passes through the gas after a jar discharge, it is positively destructive, undoing part of the work which has been done by the jar discharge. This is illustrated by the experiment of Fig. 3. We allow a stream of the rarefied nitrogen to pass in succession through the discharge tubes A and B and the observation vessel C. The jar discharge passing in A produces active nitrogen, recognised by the orange glow. If we start an uncondensed discharge in B, leaving other conditions unchanged, the

FIG. 3.



brilliancy of the glow in C is diminished, proving the destructive effect above referred to.

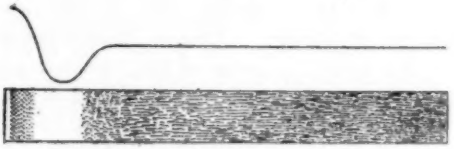
This and other evidence proves that the production of active nitrogen by the discharge is of the nature of a reversible reaction. The concentration only attains a certain limit, which may be lowered if the conditions become less favourable.

We may consider the analogy of this to better known cases of the production of endothermic substances. Consider, for instance, the known production of ozone from oxygen by the action of a high temperature. The concentration of ozone increases with the temperature of the hot tube, and the object is to cool the hot gases as quickly as possible, so as to preserve the concentration characteristic of a high temperature. If we subsequently passed the ozonised oxygen through a less strongly heated tube, we should find the concentration lowered thereby. In directing attention to this analogy, I do not wish to commit myself to the view that the action of the discharge is necessarily due to high temperature. There

are many doubts and obscurities overshadowing any theory of that kind.

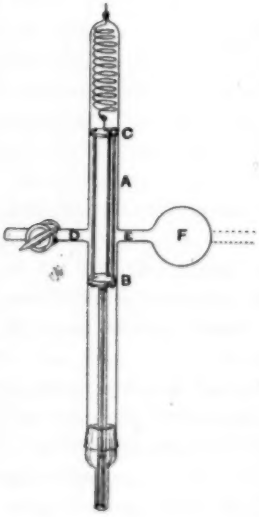
Although, as we have seen, the condensed discharge is the most efficient for activation of nitrogen, it is worth while to go back for a moment to the uncondensed discharge, or steady current through

FIG. 4.



the gas, produced preferably by means of a high-tension continuous-current dynamo. In this case, the discharge presents several distinct features. There is the Crookes's dark space near the cathode, the blue negative glow, gradually fading off to the darkness of the Faraday dark space, and then the red, positive column extending to the anode. These features are indicated in the slide (Fig. 4). We may draw a current of nitrogen transversely across any part of this discharge (the apparatus used is shown in Fig. 5) and obtain activation. As might be expected, the intensity of activation is not the same in the different parts of the discharge. The ordinates of the curve drawn above the figure of the discharge tube show the comparative intensities in the different parts of the tube, and it will be seen that the blue negative glow, particularly in the immediate neighbourhood of the cathode, is the part of the discharge where activation is strongest. It is worth noticing, and may be significant, that the bluer kind of discharge, whether obtained by approaching the cathode or by introducing a Leyden jar, is the more efficient in producing active nitrogen.

FIG. 5.



Much more might be said about the electrical conditions for producing active nitrogen, but I will pass to what, from the chemical point of view, may be of more interest. In the Royal Institution lecture in 1913, which has been mentioned, I referred to certain conclusions which Comte, and also Tiede and Domcke,

had reached in Germany. Their conclusion was that the phenomena which I had described in connexion with active nitrogen did not occur unless the gas contained traces of oxygen, and the last two authors went so far as to conclude from this that there was no such thing as active nitrogen. I said at the time that I was satisfied they were entirely mistaken as to the necessity for oxygen; but I now recognise that I spoke over confidently, and that this was too strong an expression to use. I think you will agree with me that the experiments I have shown you this evening on the formation of hydrocyanic acid and of nitrides are not easy of interpretation if the existence of active nitrogen is denied; but there was this much of truth in Tiede and Domcke's conclusion—that very pure nitrogen does not yield active nitrogen under the influence of the discharge, and that a trace of oxygen added will make it do so. What they did not discover, but what I have found since, is that a trace of almost any admixture will have the same effect. For instance, a trace of methane or ethylene will do it, or, again, carbon dioxide, or carbon monoxide, or hydrogen sulphide, or mercury vapour. In the experiments on which I relied when I denied the validity of Tiede and Domcke's work, my attention was concentrated on the removal of any trace of free oxygen; this did not result in reducing the glow, and I now appreciate that this was because other impurities were present. I was right in denying that oxygen was essential, but I was wrong in saying that pure nitrogen was all that was needed.

The method which I have generally used for preparing nitrogen is to take the commercial compressed gas, prepared by the rectification of liquid air, and to store it over water in a gas holder, in which is hung up a perforated metal bucket containing phosphorus. Gas prepared in this way always gives active nitrogen freely. To begin with, it is moist. I have always dried it with an ordinary tube of phosphoric oxide, but if the spectrum of the glow is photographed, it still shows the β- and γ-groups of bands characteristic of oxygen compounds present in active nitrogen. Passage over very long tubes tightly packed with granular phosphoric oxide reduces the intensity of these bands almost to the vanishing point.

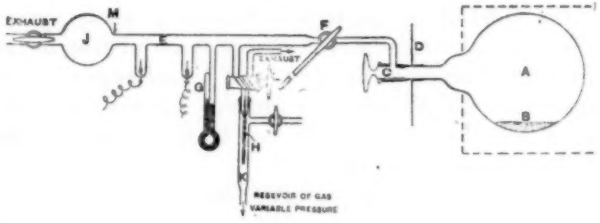
When they disappear, however, another impurity is unmasked, for the violet and ultra-violet bands characteristic of cyanogen compounds appear, showing that hydrocarbons are present, and react with the active nitrogen to yield this spectrum. I have tried to get rid of these cyanogen bands by employing specially pure phosphorus, which I owe to the kindness of Mr. Albright, but without success. We cannot get pure nitrogen by this method,

although it is fairly successful in removing oxygen and oxygen compounds.

I have not hit on any really convenient plan for getting nitrogen so free from impurities that it does not yield active nitrogen. The method that has served me best is to heat the commercial gas in a globe of 4 litres capacity for many hours at 300° with metallic sodium. It is desirable, if not absolutely necessary, to avoid using sodium which has been stored in oil, and thus contaminated with hydrocarbons. The globe once set up serves for repeated charges of nitrogen, and seems to perform better after it has been used repeatedly.

Hot sodium has the advantage of destroying nearly all the impurities that might be present in the nitrogen, for example, oxygen, water vapour, carbon dioxide, hydrocarbons. Hydrogen, it is true, is apt to be liberated, but this for the present purpose is comparatively unimportant. Gas taken from the globe *A* (Fig. 6) (which is allowed to cool after the purifying process is

FIG. 6.



over) is led through the discharge tube *E* and the bulb *J*, when, if any active nitrogen is produced, we shall see the characteristic glow. The glow from the gas purified in this way may be got very faint, verging on invisibility, and we can then restore it by admission of a suitable impurity in very minute amount through the capillary tube *H*. The exact manipulation in connexion with this admission of the gas need not detain us now; I have described it in one of my Royal Society papers. The general method is to increase the feed at the outer end of the capillary from low pressure towards atmospheric pressure until the effect becomes appreciable.

The flow of nitrogen was regulated by hand, so as to maintain a rate of 2·6 litres per hour, and the tributary stream through the fine capillary could be compared with this, so as to show what fraction of impurity was being added. With oxygen, for instance, the effect was perceptible with a tributary stream of 1 c.c. per hour, and 3·5 c.c. produced the maximum effect. In the latter case, the oxygen added was 1/750th part of the whole. If we add

much more oxygen than this, the yellow glow begins to be spoilt, and 2 per cent. admixture destroys it altogether.

As I have explained, oxygen is not the only admixture that brings in the yellow glow again. Among gases that do not contain oxygen, hydrogen sulphide, ethylene, and methane will do the same. Methane acted when present in very small concentrations. It had a perceptible effect when only 1/30,000th part was added to the nitrogen stream.

I have seen a criticism of these experiments in which it is suggested that no sufficient precautions were taken to guard against traces of oxygen or oxygen compounds in these added gases. This criticism does not seem to be well considered. If, for instance, we supposed the "methane" (which, as a matter of fact, was carefully prepared from aluminium carbide and purified by liquefaction and fractional evaporation) to *consist entirely of pure oxygen*, the observed facts would not be covered, for the methane added in the experiment just cited was only about 1/10th of the minimum amount of oxygen required to produce an observable effect.

This action of foreign substances in encouraging the production of active nitrogen is very mysterious, although not perhaps more so than the necessity for minute traces of water in many commonplace chemical reactions, which has been so admirably established by my colleague, Prof. Baker. I was at one time hopeful of connecting it with a change in the conditions of the electric discharge, and it is true that the introduction of a trace of oxygen, for example, considerably increases the drop of potential over the cathode at the same time that it increases the yield of active nitrogen. On the other hand, we may arrange so that the stream of nitrogen gas does not reach the cathode, but is led away after being exposed to the positive part of the discharge only. In this case, we find that a trace of oxygen produces the usual favourable effect on the generation of active nitrogen without at all affecting the electrical conditions in that part of the discharge which is operative.

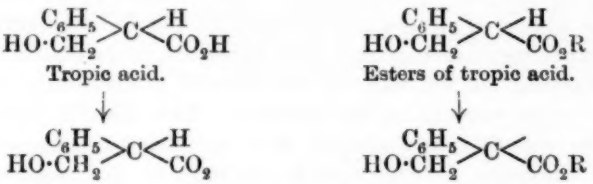
The whole of this part of the subject requires further study; and, in conclusion, I must admit that investigations, now lasting more than seven years, have only touched the fringe of the subject.

XXIV.—*Studies in the Phenylsuccinic Acid Series. Part VI. Racemisation Phenomena Observed during the Investigation of the Optically Active Phenyl- and Diphenyl-succinic Acids and their Derivatives.*

By Henry Wren.

It has been recently shown (Wren and Still, T., 1917, **111**, 1019) that the esters of *r*- and *meso*-diphenylsuccinic acids are interconvertible under the influence of alkali. To quote a specific example, ethyl *r*-diphenylsuccinate is almost quantitatively transformed into the ester of the *meso*-acid when its alcoholic solution is treated with a solution of sodium ethoxide in ethyl alcohol; also, when the ester is hydrolysed with an insufficient amount of aqueous ethyl-alcoholic potassium hydroxide solution, the non-hydrolysed portion is found to have suffered partial isomerisation, with the production of ethyl *meso*diphenylsuccinate. Since, in solution at any rate, ethyl *r*-diphenylsuccinate may be regarded as a molecular mixture of ethyl *d*-diphenylsuccinate and ethyl *l*-diphenylsuccinate, it was to be expected that the esters of the optically active acids would separately undergo similar transformation, and would therefore become racemised, the possibility of a balanced action being excluded in this case, since any further isomerisation of the *meso*-ester which might be formed would merely lead to the production of the *r*-ester. The theoretical expectations have been fully confirmed by a series of experiments with the methyl and ethyl esters of the optically active acids. A typical example is furnished by the formation of ethyl *meso*-diphenylsuccinate as a product of the action of ethyl-alcoholic sodium ethoxide on ethyl *l*-diphenylsuccinate. Similarly, when ethyl *d*-diphenylsuccinate is hydrolysed with an insufficient amount of aqueous ethyl-alcoholic potassium hydroxide solution, the non-hydrolysed portion is found to be almost inactive towards polarised light and to consist practically entirely of ethyl *meso*diphenylsuccinate. It would thus appear that the racemisation previously observed to occur during the hydrolysis of esters of the optically active diphenylsuccinic acids (Wren and Still, T., 1915, **107**, 1454) takes place in part, at any rate, previous to the actual hydrolysis, and is thus due to rearrangement of the ester, and not of the acid. The greater liability of esters as compared with the corresponding acids to racemisation under the influence of alcoholic alkali has been pointed out by Gadamer (*Chem. Zeit.*, 1910, **34**, 1004; *J. pr.*

Chem., 1913, [ii], **87**, 312), who found that, whilst the esters of tropic acid are readily racemised, the acid itself is not racemised by hydroxyl ions. This difference in behaviour is ascribed to the ionisation of the acid at the carboxyl group, whilst the ester, which behaves as a pseudo-acid, only becomes ionised in the presence of hydroxyl ions, thus:



It has, however, been pointed out by Frankland (T., 1913, **103**, 725) that the racemisation may be due to loss of asymmetry caused by tautomeric change previous to ionisation, thus:

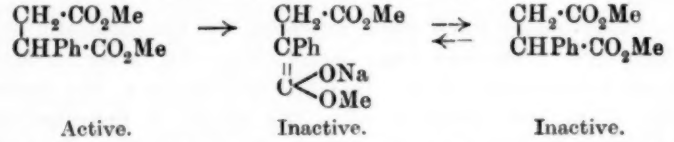
The only instance of racemisation of an ester previous to hydrolysis which appears to have been noted in the literature is the observation of McKenzie and Widdows (T., 1915, **107**, 713) that *l*-menthyl *d*-phenyl-*p*-tolylacetate is, in part, catalytically racemised by alkali prior to its undergoing hydrolysis. In a case which presents some analogies, Wren (T., 1909, **95**, 1596) found that the portion of the ester which escapes conversion into amide is partly inactivated when methyl *l*-mandelate is acted on by cold alcoholic ammonia.

The observations have been extended to the optically active phenylsuccinic acids and their esters, since the latter substances are much more readily soluble than the derivatives of the diphenylsuccinic acids, and therefore allow the course of racemisation to be followed directly by polarimetric measurement. It is thus found that ethyl and methyl *d*-phenylsuccinates are rapidly and completely racemised by the action of a solution of the requisite sodium alkyloxide in the corresponding alcohol, and also that when the latter ester is treated with potassium hydroxide dissolved in slightly aqueous ethyl alcohol in quantity insufficient for complete hydrolysis, the non-hydrolysed portion is almost completely racemised under the conditions described in the experimental section of the paper.

Some time ago, it was found by Wren and Williams (T., 1916, **109**, 579) that a partly racemised acid was obtained when methyl *d*-phenylsuccinate is hydrolysed by an excess of aqueous ethyl-

alcoholic potassium hydroxide solution. Thus, in one experiment, the ester was heated with about six times the theoretically necessary quantity of potassium hydroxide dissolved in aqueous ethyl alcohol (water : alcohol : : 1 vol. : 2 vols.), when the recovered acid was found to have $[\alpha]_D$ +110·2° in acetone solution, whilst the parent acid had $[\alpha]_D^{12\cdot5}$ +175·4°. The considerable activity of this acid became somewhat remarkable when considered in conjunction with the almost complete racemisation of the non-hydrolysed ester in the experiment just quoted, and pointed to a profound influence of the varying factors, namely, the amount of potassium hydroxide and the water content of the solution. The effect of variation in the latter was therefore studied, and was found to exercise a very marked influence on the optical activity of the recovered acid. In three strictly comparable experiments, in which the only differences consisted in the use of absolute, approximately 80 per cent. and 50 per cent. alcohol respectively, the acid formed by hydrolysis was found to have $[\alpha]_D$ +3·1°, +59·1°, and +100·3° respectively in ethyl-alcoholic solution in which the parent acid had $[\alpha]_D$ +147·4°; under closely similar conditions, the latter acid was found to be unaffected by the action of an excess of alcoholic or aqueous-alcoholic sodium hydroxide solution.

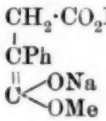
During the last few years, a considerable amount of evidence has been accumulated which indicates that racemisation under the influence of alkali may frequently be attributed to keto-enolic desmotropy, with consequent disappearance of the asymmetry of the compound. In the present instance, the inactivation of methyl *d*-phenylsuccinate when acted on by sodium methoxide may be due to the formation of the enolic form, thus:



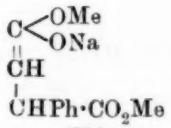
Active. Inactive. Inactive.

The evidence which has been brought forward in favour of such an explanation of racemisation in analogous case is, so far, of a purely qualitative nature; in no single instance has the enolic form been isolated or its amount determined. The actual separation of the enolic modification would doubtless be a matter of great difficulty in many cases, since the proportion of enolised molecules need be but infinitesimal to account for the phenomena of racemisation. On the other hand, it was hoped to be able to bring quantitative evidence of the presence of the enolic modification by utilising the method adopted by K. H. Meyer (*Ber.*, 1912, **45**, 2864) in his investigations on ethyl malonate and ethyl

methanetricarboxylate. Direct titration of a methyl-alcoholic solution of methyl *d*- or *r*-phenylsuccinate with bromine failed to disclose the presence of any enol, and a similar result was obtained when experiments were performed on the esters dissolved in methyl-alcoholic sodium methoxide solution, although under the latter conditions ethyl malonate was found to be largely enolised. The experimental conditions were not greatly varied in this case, however, since the objection could possibly be raised that, in order to demonstrate the point at issue, it would be necessary to show definitely that enolisation occurs in such a manner as to form compound I, and not II:



(I.)



(II.)

It is hoped to apply the method, however, to esters of certain monobasic acids to which this objection cannot be urged.

Lastly, if racemisation be attributable to the formation of an enolic derivative, it would be expected that the nature of the basic atom or group of the alkali would have an influence on the result. Experiments on the hydrolysis of methyl *d*-phenylsuccinate with aqueous ethyl-alcoholic tetramethylammonium hydroxide solution were therefore performed; racemisation was found to be even more pronounced than with potassium hydroxide solution under nearly similar conditions.

Experimental.

Formation of Ethyl meso*Diphenylsuccinate from Ethyl* d- *and* l-*Diphenylsuccinates.*

A. *By the Action of Ethyl-alcoholic Sodium Ethoxide Solution.*—Ethyl *l*-diphenylsuccinate (1 gram) was warmed with a solution of sodium ethoxide in ethyl alcohol (0·666*N*; 20 c.c.) in a closed vessel to about 50°, when it dissolved completely; the solution was allowed to cool to the ordinary temperature, when it became almost solid. After remaining during three days at the temperature of the laboratory, the precipitate was removed and washed successively with alcohol, warm water, and, finally, alcohol. It melted at 139—140°, and was optically inactive in acetone solution. After being crystallised from rectified spirit, ethyl *meso*diphenylsuccinate was obtained in well-defined needles melting at 140—141°.

B. *By Partial Hydrolysis.*—Ethyl *d*-diphenylsuccinate (1·5

grams) was heated during four hours with aqueous ethyl-alcoholic potassium hydroxide solution (0·25*N*; 15 c.c.), this being about three-fifths of the quantity required for complete hydrolysis. The solution was diluted with water, and the unattacked esters were extracted with chloroform. The residue, obtained after removal of the latter, melted at 138—140°; it had $[\alpha]_D$ +5·4° in acetone solution ($l=2$, $c=1·113$, α_D +0·12°), whereas the pure *d*-ester has $[\alpha]_D^{16}$ +279·4° under similar conditions. After being crystallised from rectified spirit, it yielded pure ethyl *meso*diphenylsuccinate, which was optically inactive in acetone solution and melted at 140—141°.

Formation of Methyl meso*Diphenylsuccinate from Methyl* l- *and* d-*Diphenylsuccinates.*

A. *By the Action of a Methyl-alcoholic Solution of Sodium Methoxide.*—Methyl *l*-diphenylsuccinate (1 gram) was heated in a stoppered flask during four hours at 55—65° with a solution of sodium methoxide in absolute methyl alcohol (0·704*N*; 60 c.c.). When the solution was cooled, a quantity of fine, prismatic crystals separated, which were removed, washed with water and methyl alcohol, and dried. After being crystallised from acetone, the product was obtained in well-defined needles, which were optically inactive when dissolved in chloroform ($l=2$, $c=0·5115$), and were identified as methyl *meso*diphenylsuccinate by their crystalline form, melting point (218·5—219·5°) alone, and when mixed with an approximately equal quantity of the synthetic *meso*-ester.

B. *By Partial Hydrolysis.*—A solution of methyl *l*-diphenylsuccinate (1·5 grams) in boiling methyl alcohol (100 c.c.) was heated during four hours with aqueous methyl-alcoholic potassium hydroxide solution (0·593*N*; 8 c.c.), this being approximately half the quantity of alkali required for the complete hydrolysis of this amount of the ester. The alcohol was removed on the water-bath and the residue warmed with water. The undissolved portion was removed and dried. It was optically inactive when dissolved in chloroform ($l=2$, $c=0·8365$), and, after being crystallised from acetone, yielded methyl *meso*diphenylsuccinate, which melted at 218·5—219·5°; the melting point was unaltered by admixture with the synthetic *meso*-ester.

Racemisation of Methyl and Ethyl d*-Phenylsuccinates under the Influence of Alkali.*

A. *By Sodium Alkyloxide.*—Methyl *d*-phenylsuccinate (0·8157 gram) was dissolved in methyl-alcoholic sodium methoxide solution (20·5 c.c.), and transferred as rapidly as possible to a 2-dcm. tube. Approximately three minutes after being prepared, the solution had α_D +8°, but the field was somewhat cloudy, and the activity altered too rapidly to allow of accurate measurement. After about fifteen minutes, the value had decreased to +3·5°, after forty minutes to +0·5°, after seventy minutes to +0·17°, after one hundred minutes to +0·05°. After two hours, the solution was poured into a slight excess of dilute hydrochloric acid. The ester was extracted with ether, the ethereal solution washed with sodium carbonate, and dried over calcium chloride. The residue, obtained after removal of the solvent, solidified readily, and was optically inactive in acetone solution ($l=2$, $c=1·555$). After being crystallised from light petroleum, it yielded characteristic clusters of prisms of methyl *r*-phenylsuccinate, which melted at 57·5—58·5°. The melting point remained unchanged when the substance was mixed with the synthetic *r*-ester.

In a similar manner, ethyl *d*-phenylsuccinate (0·9964 gram) was dissolved in ethyl-alcoholic sodium ethoxide solution (1·059*N*; 20 c.c.). In this case, racemisation proceeded so rapidly as to be almost complete before polarimetric measurements could be made, and the solution had become quite inactive within ten minutes. Since the liquid nature of the ethyl *r*-ester rendered the identification of a small quantity of it a matter of difficulty, water was added to the solution, and the ester hydrolysed. The resulting *r*-phenylsuccinic acid melted at 167—168°, whereas Higson and Thorpe (T., 1906, **89**, 1470) give 168° as the melting point of this acid.

B. *By Partial Hydrolysis.*—Methyl *d*-phenylsuccinate (3 grams) was heated to boiling during two and a-half hours with slightly aqueous methyl-alcoholic potassium hydroxide solution (0·395*N*; 25 c.c.), this being rather more than one-third of the quantity theoretically necessary for complete hydrolysis. The alcohol was removed on the water-bath, and the residue mixed with water and shaken with ether. The residue (about 0·3 gram) obtained after removal of the ether solidified readily, and had $[\alpha]_D$ +2·12° when dissolved in acetone ($l=2$, $c=1·178$, α_D +0·05°), whereas the pure ester has $[\alpha]_D^{10}$ +152·2° under similar conditions. After being crystallised from light petroleum (b. p. 40—60°), it yielded pure

methyl *r*-phenylsuccinate, which melted at 57—58·5°; this value remained unchanged after admixture with the synthetic ester.

Action of Alkali on l-*Phenylsuccinic Acid.*

The *l*-phenylsuccinic acid used in these experiments had $[\alpha]_D$ −148·3° in ethyl-alcoholic solution, a value which agrees well with the data of Wren and Williams (*loc. cit.*).

Three comparative experiments were performed, in which the acid (1 gram) was treated in a closed vessel with (*a*) sodium ethoxide solution (1·059*N*; 50 c.c.) and absolute ethyl alcohol (20 c.c.); (*b*) sodium ethoxide solution (50 c.c.), alcohol (20 c.c.), and water (0·95 c.c.), and (*c*) sodium ethoxide solution (50 c.c.), alcohol (10 c.c.), and water (10 c.c.). In each case a certain amount of precipitate separated. The mixtures were heated with frequent agitation during five hours at 70°, then neutralised with hydrochloric acid, and evaporated to remove alcohol; the acids were isolated by extraction of the acidified solutions with ether. The dried acids were polarimetrically examined in ethyl-alcoholic solution, the values for the specific rotations being (*a*) −146·6° (l=2, c=2·8815, α_D −8·45°), (*b*) −145·5° (l=2, c=1·691, α_D −4·92°), and (*c*) −146·2° (l=2, c=1·7035, α_D −4·98°). In no case, therefore, was any evidence of racemisation obtained.

Complete Hydrolysis of Methyl d-*Phenylsuccinate by Alcoholic Sodium Hydroxide containing differing Proportions of Water.*

In these experiments, the weight of ester and alkali, the total volume of the solution, the temperature, and duration were maintained uniform, the only variation consisting in the replacement of differing volumes of alcohol by water. Stock solutions of ester were prepared by dissolving 2 grams of the latter in 30 c.c. of ethyl alcohol, and of alkali by dissolving sodium in absolute ethyl alcohol; the latter solution was 1·1*N*. Ten c.c. of the ester solution were mixed with (*a*) alkali solution (25 c.c.), alcohol (25 c.c.), and water (0·45 c.c.); (*b*) alkali solution (25 c.c.), alcohol (15 c.c.), water (10 c.c.), and (*c*) alkali solution (25 c.c.), water (25 c.c.). The solutions were heated in closed flasks during four hours at 60—65°; precipitates speedily separated in (*a*) and (*b*) but (*c*) remained homogeneous throughout. The resulting mixtures were nearly neutralised with hydrochloric acid and evaporated to remove alcohol; the aqueous solutions were extracted with ether after acidification with mineral acid. The residual phenylsuccinic acids were polarimetrically examined in ethyl-alcoholic solution, when

the following values were observed for the specific rotation: (*a*) +3·1° (*l*=2, *c*=2·2391, α_D +0·14°); (*b*) +59·1° (*l*=2, *c*=1·913, α_D +2·26°); (*c*) +100·3° (*l*=2, *c*=2·0731, α_D +4·16°).

Complete Hydrolysis of Methyl d-*Phenylsuccinate by Aqueous-Alcoholic Tetramethylammonium Hydroxide Solution.*

The solution of the alkali was prepared by warming an aqueous solution of tetramethylammonium iodide with a slight excess of silver oxide, and removal of silver iodide and unchanged oxide. The filtrate was concentrated to 14 c.c., and then diluted with ethyl alcohol to 55 c.c. An approximately *N*-solution was thus obtained.

The methyl *d*-ester (1 gram) was heated during two and a-half hours with the solution described above, and the corresponding acid isolated in the usual manner; it melted at 164—168·5°, and had $[\alpha]_D$ +10·1° in ethyl-alcoholic solution (*l*=2, *c*=3·329, α_D +0·67°).

Action of Ferric Chloride on Methyl d-*Phenylsuccinate.*

It has been shown by Meyer (*Ber.*, 1911, **44**, 2725) in the case of ethyl acetoacetate that ferric chloride exerts a direct enolising action. The behaviour of an ethyl-alcoholic solution of methyl *d*-phenylsuccinate towards anhydrous ferric chloride has therefore been polarimetrically investigated in the expectation that enolisation, if induced at the asymmetric carbon atom, would betray itself by racemisation. The solutions, however, were found to be optically stable under these conditions.

Methyl *d*-phenylsuccinate (0·4869 gram) was dissolved in ethyl alcohol and the solution made up to 20 c.c.; a portion of this solution had α_D +6·73° when examined in a 2-dcm. tube, and this value had not changed at the end of forty hours after the addition of a small quantity of ferric chloride. A further portion of the latter substance was added, and the solution allowed to remain at the temperature of the laboratory during nine days, at the end of which period the ester was isolated and examined in ethyl-alcoholic solution; it had $[\alpha]_D$ +129·8°, whereas the value +138·2° had been determined for the original specimen.

Possible Enolisation of Methyl Phenylsuccinate in Solution.

Methyl *d*-phenylsuccinate (0·5369 gram) and methyl *r*-phenylsuccinate (0·4496 gram) were separately dissolved in methyl alcohol

(20 c.c.) and titrated with an $N/10$-solution of bromine in the same solvent until a faint, permanent, yellow coloration was produced; 0·55 c.c. of bromine was required in each case, whilst in a blank experiment 0·60 c.c. was necessary.

Methyl *d*-phenylsuccinate (0·3292 gram) was dissolved in a well-cooled methyl-alcoholic solution of sodium methoxide, and the product poured into an excess of a solution of bromine in methyl alcohol containing hydrogen chloride. Excess of bromine was removed by the addition of β-naphthol dissolved in methyl alcohol, and the resulting solution warmed after addition of aqueous potassium iodide (10 per cent.). The liberated iodine required 0·3 c.c. of $N/10$-sodium thiosulphate solution, this quantity being the same as that required in a blank experiment.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed a part of the cost of the investigation.

MUNICIPAL TECHNICAL INSTITUTE,
BELFAST. [*Received, February 20th*, 1918]

XXV.—*Synthesis of* 3:4-*Dihydroxyphenanthrene* (*Morphol*) *and of* 3:4-*Phenanthraquinone.*

By GEORGE BARGER.

Two years ago a note was published (T., 1916, **109**, 568) describing the preparation of 3-phenanthrol-4-aldehyde, first carried out at my suggestion by a former pupil, the late J. W. Smith. As there indicated, I was able to deduce the constitution of the aldehyde from its conversion into 3:4-dihydroxyphenanthrene (morphol). From this, 3:4-phenanthraquinone was subsequently obtained, and since there has been no opportunity of further experiment in this direction, the preparation of these two compounds is described below. Morphol had not yet been synthesised, and was only known as a degradation product of morphine, for although Pschorr and Simuleanu (*Ber.*, 1900, **33**, 1810) prepared its dimethyl ether by Pschorr's well-known general method, they were unable to demethylate this compound without reduction; on boiling with hydriodic acid they only obtained 3-phenanthrol.

EXPERIMENTAL.

3:4-*Dihydroxyphenanthrene* (Morphol).

Ortho- and para-hydroxyaldehydes may be converted, often quantitatively, into the corresponding diphenols by a reaction due to Dakin (P., 1909, **25**, 194; *Amer. Chem. J.*, 1909, **42**, 477). In spite of its convenience and wide applicability, this reaction has, strangely enough, received very little attention. Dakin dissolves the aldehyde in one equivalent of sodium hydroxide and adds a molecular proportion of dilute hydrogen peroxide, when oxidation takes place at once with distinct evolution of heat. On applying the reaction to 3-phenanthrolaldehyde, the sparing solubility of the sodium salt made it necessary to work in very dilute solution, and only a minute quantity of the diphenanthrol was at first obtained. This difficulty was readily overcome by working in pyridine solution and limiting the amount of water as far as possible by the use of highly concentrated potassium hydroxide and hydrogen peroxide, as follows.

3-Phenanthrolaldehyde (1·11 grams) was dissolved in pyridine (10 c.c.) in a flask provided with a dropping funnel and exit tube, and after the air had been displaced by hydrogen, 0·55 c.c. of 30·8 per cent. hydrogen peroxide and then 0·45 c.c. of 12·5 *N*-potassium hydroxide were added through the tap funnel, which was washed out by a few drops of water. The addition of the potassium hydroxide caused a considerable rise in temperature (but hydrogen peroxide alone, with pyridine, does not react). After boiling for a few seconds, the solution was cooled and excess of hydrochloric acid was added through the funnel. The solution was then extracted with ether, and the ethereal extract washed free from pyridine with acid. On evaporation of the ether, the dihydroxyphenanthrene crystallised; the yield of the crude product was 1·05 grams. It was dissolved in 5 c.c. of boiling benzene, when, on cooling, 0·61 gram separated in almost colourless crystals, and a further 0·22 gram was obtained by adding light petroleum to the mother liquor, the total yield of pure substance thus amounting to 80 per cent. of the theoretical. The substance so obtained was very sensitive to oxidation; it instantly reduced silver nitrate in neutral solution at the ordinary temperature. A trace of ferric chloride gave a reddish-brown coloration, but excess caused oxidation. It was recrystallised from water and from petroleum, b. p. 80—90°, and then melted at 142—143°, so that it seemed to be identical with morphol (O. Fischer and Vongerichten, *Ber.*, 1886, **19**, 793, give 143°). By recrystallisation, it was obtained almost,

but not quite colourless. A perfectly colourless specimen resulted on sublimation in the vacuum of a Gaede pump at 130°, but the sublimate melted at 142°. On acetylation by boiling with acetic anhydride and a trace of sulphuric acid, an acetyl compound was obtained, which, after crystallisation from petroleum, b. p. 80—90°, and then from methyl alcohol, melted at 158° (O. Fischer and Vongerichten give 159° as the melting point of diacetylmorphol).

Since no morphol was available for direct comparison, the diphenol was methylated in order to provide a conclusive proof of its identity, for both the possible dimethyl ethers, 2:3- and 3:4-dimethoxyphenanthrene, have been synthesised by Pschorr and his pupils.

The crude oxidation product from 1·11 grams of the hydroxyaldehyde was dissolved in 10 c.c. of methyl alcohol and 0·85 c.c. of methyl sulphate (2 molecular proportions), and 0·72 c.c. of 12·5*N*-potassium hydroxide were added alternately four times. After adding ether, washing with sodium hydroxide, drying, and evaporating the ether, the residue was distilled twice under 12 mm. pressure. At first, crystallisation could not be induced, but a trace crystallised from methyl alcohol on spontaneous evaporation of the solvent, and on adding this to the main bulk, the whole solidified almost completely. The crystals were drained on a tile, the yield was 0·3 gram. When recrystallised from methyl alcohol by evaporation at the ordinary temperature, narrow, rectangular plates were obtained melting at 45°. The picrate formed ruby-red crystals melting at 105—106°, and the dibromo-derivative colourless needles melting at 124—125°. The melting points of 3:4-dimethoxyphenanthrene, its picrate, and its dibromo-derivative are given by Pschorr and Simuleanu (*Ber.*, 1900, **33**, 1810) as 44°, 105—106°, and 124—125° respectively, and those of the corresponding 2:3-derivatives by Pschorr and Buckow (*Ber.*, 1900, **33**, 1829) as 131°, 127—128°, and 160° respectively, so that the diphenol is identified with certainty as 3:4-dihydroxyphenanthrene and the aldehyde, from which it is derived, as 3-phenanthrol-4-aldehyde.

3:4-*Phenanthraquinone*, $C_{14}H_8O_2$

Having found a comparatively ready method of preparing morphol, I was able to oxidise it to the corresponding quinone by Willstätter and Pfannenstiehl's method (*Ber.*, 1904, **37**, 4744). Five grams of silver nitrate were decomposed in a stoppered cylinder with the calculated quantity of sodium hydroxide, and the silver oxide was washed by decantation twelve times with water, six

times with acetone, and six times with dry ether. Then an ethereal solution of 0·8 gram of morphol was added, together with 2 grams of anhydrous sodium sulphate, and the mixture was shaken for fifteen seconds. A blood-red solution was formed at once, and, after settling, was decanted; the silver oxide was extracted repeatedly with ether until the solvent was no longer coloured red. On evaporation, the quinone crystallised. It was dissolved in 25 c.c. of boiling benzene, when, on cooling, 0·52 gram separated, or 65 per cent. of the theoretical. A little more was obtained by concentrating the mother liquor and adding light petroleum. 3 : 4-*Phenanthraquinone* was thus obtained in brilliant red, short, pointed prisms. The melting point is not sharp; at 125—130° the substance blackens, and on rapid heating melts in the neighbourhood of 132—133°:

0·1412 (dried at 100°) gave 0·4167 CO_2 and 0·0501 H_2O. C = 80·5; H = 3·9.

$C_{14}H_8O_2$ requires C = 80·8; H = 3·9 per cent.

The substance is a true derivative of *o*-benzoquinone, resembling 1 : 2-naphthaquinone rather than 9 : 10-phenanthraquinone in colour and instability. It further differs from 9 : 10-phenanthraquinone in not yielding Laubenheimer's reaction.

It is at once reduced by sulphurous acid to morphol. In the oxidation of the latter with silver oxide, no isomeric colourless form of the quinone could be observed, as in the case of *o*-benzoquinone (Willstätter and Müller, *Ber.*, 1908, **41**, 2580). It was easy to repeat their experiments with catechol, but not with morphol.

The phenanthrene employed in making the above substances was purchased with a grant from the Research Fund of the Chemical Society, for which grateful acknowledgment is made.

LISTER INSTITUTE OF PREVENTIVE MEDICINE,
CHELSEA GARDENS, LONDON, S.W. [*Received, March 19th*, 1918.]

XXVI.—*The Alkaloids of Ipecacuanha. Part III.*

By Frank Lee Pyman.

In the previous paper of this series (T., 1917, **111**, 424), it was shown that *O*-methylpsychotrine gave a mixture containing emetine and *iso*emetine* on reduction. The formation of *iso*emetine was demonstrated by the isolation of its benzoyl derivative, for neither *iso*emetine nor any of its salts had at that time been obtained in a crystalline form. Later, however, the *hydrobromide* became crystalline, and was readily purified by crystallisation from water, and, from the pure salt, the *base*, *hydrochloride*, and *hydrogen oxalate* were prepared in the usual manner, and also obtained in crystalline form. On benzoylation, the base gave the benzoyl*iso*emetine previously described. Since emetine and *iso*emetine are produced by the reduction of methylpsychotrine, it was to be expected that *iso*emetine, like emetine, could be oxidised to methylpsychotrine and rubremetine, and this proved to be the case. The view that emetine and *iso*emetine are stereoisomerides was thus confirmed, and it appeared to be of interest to determine whether an equilibrium between the two bases could be established by boiling with amyl alcohol and sodium amyloxide. Experiments to this end were unsuccessful, for, after fourteen hours' boiling, no evidence of partial racemisation was obtained, each base being recovered unchanged except in so far as it had been hydrolysed to phenolic bases.

The fact that psychotrine gives cephaeline and *iso*cephaeline on reduction, whilst the methyl ether of psychotrine gives emetine and *iso*emetine, indicated the probability that *iso*emetine was the methyl ether of *iso*cephaeline, and this has now been proved by preparing *iso*emetine by the methylation of *iso*cephaeline.

When methylated under suitable conditions, *iso*emetine gives a well-crystallised *N*-methyl derivative, N-*methyl*iso*emetine*, which proves to be the *O*-methyl ether of the isomeride of *N*-methylcephaeline previously described (T., 1914, **105**, 1624); this substance is therefore N-*methyl*iso*cephaeline*.

* The term *iso*emetine is clearly appropriate to this compound, which is the methyl ether of the *iso*cephaeline described in 1914 (Carr and Pyman, T., 1914, **105**, 1591), and the parent of the substance already named benzoyl-*iso*emetine (Pyman, T., 1917, **111**, 424). It has since been employed by Karrer (*Ber.*, 1917, **50**, 582) for a reduction product of rubremetine. Whilst the coincidence is unfortunate, it does not appear to be important, for Karrer's '*iso*emetine'—an amorphous base from which no crystalline derivatives were prepared—is probably a mixture of stereoisomerides.

Complete methylation of *iso*emetine yields a well-crystallised *N-methyl*iso*emetine methiodide*, which is accompanied by an amorphous salt. This is probably a mixture of the two stereoisomeric methiodides of *N*-methyl*iso*emetine, the isomerism of which depends on the presence of an asymmetric nitrogen atom, for it is shown later that the complete methylation of emetine leads to a similar result. This view is borne out by the fact that the crystalline and amorphous salts give *N-methyl*iso*emetinemethine* in equally good yield when converted into the corresponding methohydroxides and evaporated in a vacuum. This methine, like that of emetine, crystallises well as the neutral *oxalate*, and also forms a well-crystallised *methiodide*. So far, attempts to effect its further degradation have not led to crystalline products.

The connexion between the compounds described above and their relation to the compounds described in the previous papers is shown in the diagram on p. 225.

Reference has been made above to the formation of two stereoisomeric methiodides by the complete methylation of emetine. This operation, which consists in heating emetine with methyl iodide and aqueous sodium carbonate, has been carried out previously by several authors, but hitherto only one methiodide has been isolated, although the formation of "by-products" has been observed. In view of the fact that emetine contains a tertiary nitrogen atom common to two ring complexes, the formation of two stereoisomeric *N*-methylemetine methiodides owing their separate existence to the asymmetry of this nitrogen atom appeared to be possible. On experiment, it was found that the product of the reaction gave, besides the previously known methiodide, which melts at 225—226° (corr.) and has $[\alpha]_D$ −10°, a stereoisomeride, which melts at 262° (corr.) and has $[\alpha]_D$ +68°. Proof that this is, in fact, a stereoisomeric *N*-methylemetine methiodide, and not a derivative of some impurity in the emetine employed, is afforded by the fact that it yields the same methine as does the previously known methiodide. In accordance with the usual practice (compare Scholtz, *Ber.*, 1905, **38**, 595; Voss and Gadamer, *Arch. Pharm.*, 1910, **248**, 43; Jowett and Pyman, T., 1913, **103**, 290), the salt of lower melting point is termed the α-salt, that of higher melting point the β-salt. In previous cases, it has been possible to convert the α-salt into the β-salt by heating it above its melting point. α-*N*-Methylemetine methiodide, however, effervesces at its melting point and probably undergoes decomposition, for none of the β-salt could be isolated from the reaction product.

The remarkable influence of stereochemical structure on physiological action, which has been observed in many other cases, is

apparent in the case of emetine and *iso*emetine, which differ only in the sign of one asymmetric carbon atom.

Dr. H. H. Dale, F.R.S., of the staff of the Medical Research Committee, has kindly determined the relative toxicity of these compounds, and finds that *iso*emetine is rather less than half as toxic as emetine. The results of intravenous administration of different doses of their hydrochlorides to rabbits were as follows:

Emetine hydrochloride.				isoEmetine hydrochloride.			
4·25 mgm.*	per kilo.		—All died.	9·0 mgm.*	per kilo.		—All died.
4·0	,,	,,	—4 died out of 5.	8·5	,,	,,	—4 died out of 6.
3·75	,,	,,	—1 died out of 4.	8·25	,,	,,	—3 died out of 6.
3·5 or less		,,	—All lived.	8·0	,,	,,	—1 died out of 4.
				7·5 or less		,,	—All lived.

* Of the anhydrous salt.

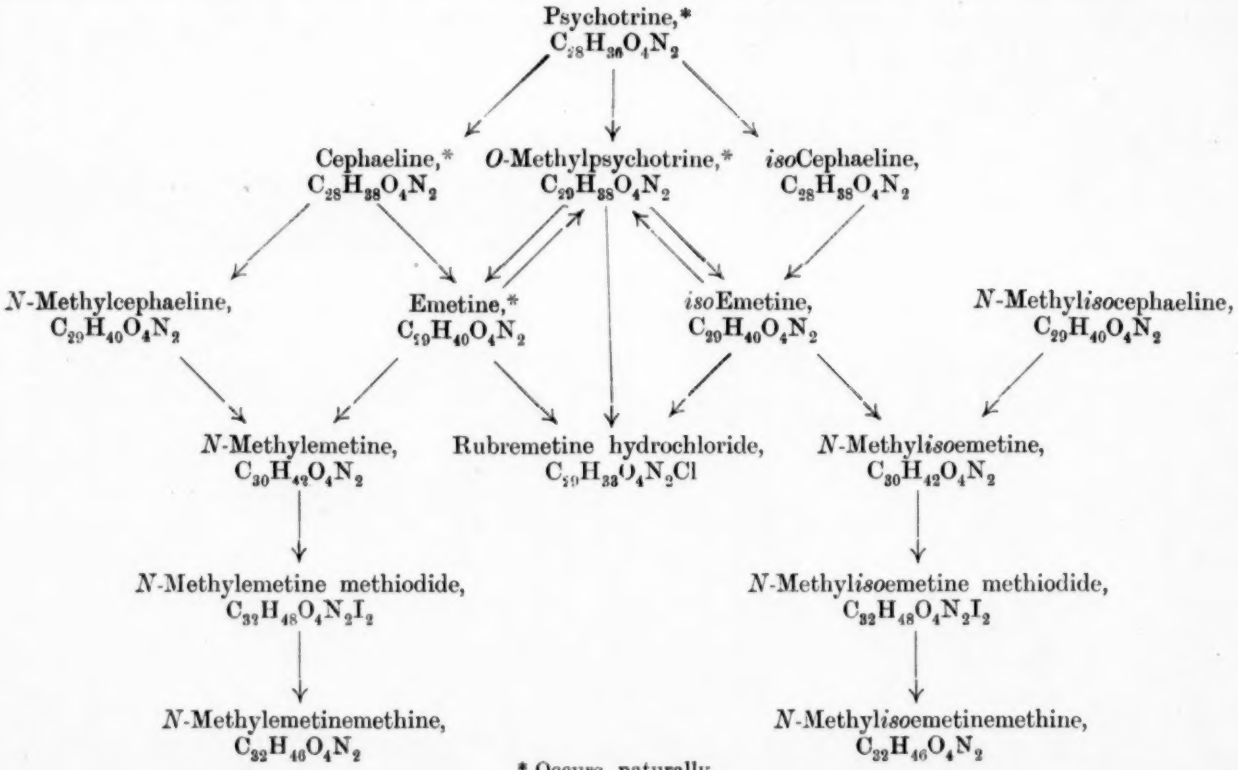
With both compounds, death resulted from acute heart failure. It was also found that *iso*emetine was practically non-emetic for cats.

A clinical trial of *iso*emetine has been carried out by Dr. G. C. Low, to whom the author's thanks are due. Whilst emetine given in amœbic dysentery nauseates the patient, but brings about the elimination of the amœbæ, Dr. Low finds that *iso*emetine is well tolerated in comparatively large doses, but does not appear to have any effect on the amœbæ.

Experimental.

Isolation of iso*Emetine.*

*iso*Emetine occurs together with emetine and base "C" amongst the reduction products of methylpsychotrine. In order to isolate it, the syrupy base recovered from the mother liquors of emetine hydrobromide (T., 1917, **111**, 439, line 10) is dissolved in alcohol (2 parts) and mixed with a solution of hydrated oxalic acid (0·5 part) in alcohol (5 parts), and kept for several days, when a spongy, crystalline mass slowly separates. This is collected and washed with alcohol, when crude *iso*emetine hydrogen oxalate remains. Further quantities remain in the mother liquors from the crystallisation of the hydrogen oxalate of base "C" (*ibid.*, p. 438). The crude hydrogen oxalate is dissolved in water, and the base regenerated into ether by sodium hydroxide; after removing the solvent, the residue is dissolved in a slight excess of dilute hydrobromic acid, digested with animal charcoal, and filtered, when *iso*emetine hydrobromide separates on inoculating and cooling, and is purified readily by recrystallisation from water.



* Occurs naturally.

iso*Emetine*, $C_{29}H_{40}O_4N_2$.

The base crystallises from ether in characteristic disks (circular plates) formed of radiating needles, containing $1H_2O$, which is not completely lost in a vacuum. The air-dried base softens at 92° and melts at 97—98° (corr.); the same form and melting point were observed after recrystallisation of the base from ethyl acetate.

Found, in air-dried base (from ether): C = 69·7; H = 8·5; loss in a vacuum = 2·5.

$C_{29}H_{40}O_4N_2,H_2O$ (498·5) requires C = 69·9; H = 8·5; loss of $1H_2O$ = 3·6 per cent.

The base is insoluble in water, but easily soluble in the usual organic solvents with the exception of light petroleum. Its colour-reactions with Fröhde's reagent (green) and sodium diazobenzene-*p*-sulphonate (red in the presence of sodium carbonate, little changed on the addition of dilute hydrochloric acid) are identical with those given by emetine.

The specific rotatory power of the base, dried in a vacuum, was determined in chloroform solution:

$$\alpha_D - 3{\cdot}33°;\ c = 3{\cdot}514;\ l = 2\text{-dcm.};\ [\alpha]_D - 47{\cdot}4°.$$

The *hydrochloride* was obtained as a mass of small needles by neutralising the base with aqueous hydrochloric acid, evaporating the solution to dryness, and boiling the residue with absolute alcohol. It melts and decomposes at 310° (corr.), and is easily soluble in water, but almost insoluble in absolute alcohol.

This salt is almost anhydrous, losing only 0·5 per cent. at 100°.

Found in dried salt: C = 62·6; H = 7·7; Cl = 12·8.

$C_{29}H_{40}O_4N_2,2HCl$ (553·4) requires C = 62·9; H = 7·7; Cl = 12·8 per cent.

The specific rotatory power of this salt was determined in aqueous solution, and found to be negative at high, but positive at low concentrations:

$$\alpha_D - 4{\cdot}70°;\ c = 15{\cdot}07;\ l = 2\text{-dcm.};\ [\alpha]_D - 15{\cdot}6°.$$
$$\alpha_D - 0{\cdot}87°;\ c = 8{\cdot}134;\ l = 2\text{-dcm.};\ [\alpha]_D - 5{\cdot}3°.$$
$$\alpha_D + 0{\cdot}38°;\ c = 4{\cdot}092;\ l = 2\text{-dcm.};\ [\alpha]_D + 4{\cdot}6°.$$
$$\alpha_D + 0{\cdot}35°;\ c = 2{\cdot}259;\ l = 2\text{-dcm.};\ [\alpha]_D + 7{\cdot}7°.$$
$$\alpha_D + 0{\cdot}23°;\ c = 0{\cdot}909;\ l = 2\text{-dcm.};\ [\alpha]_D + 12{\cdot}7°.$$

The *hydrobromide* crystallises from water in well-formed prisms, which contain $4H_2O$. It is easily soluble in hot, but sparingly so (1—2 per cent.) in cold water. After drying in a vacuum, it softens from 215° and gradually becomes transparent without flowing, up to 220° (corr.).

Found, in air-dried salt: C = 48·8; H = 7·2; loss in a vacuum, 10·1, 10·0, 10·0.

$C_{29}H_{40}O_4N_2,2HBr,4H_2O$ (714·4) requires C = 48·7; H = 7·1; H_2O = 10·1 per cent.

Found, in dried salt: C = 54·0, 54·4; H = 6·7, 6·8; Br = 24·7.

$C_{29}H_{40}O_4N_2,2HBr$ (642·3) requires C = 54·2; H = 6·6; Br = 24·9 per cent.

The specific rotatory power of the hydrated salt was determined in aqueous solution:

$\alpha_D + 0·54°$; $c = 4·153$; $l = 2$-dcm.; $[\alpha]_D + 6·5°$.
$\alpha_D + 0·42°$; $c = 1·989$; $l = 2$-dcm.; $[\alpha]_D + 10·5°$.

The *hydrogen oxalate* crystallises from water in colourless prisms, which contain $5H_2O$, and melt at 92—95° (corr.). After drying at 100°, it has no definite melting point, but softens from about 150° and effervesces at about 165° (corr.). It is easily soluble in water or alcohol, but its solution in the latter deposits a colourless, spongy mass on keeping.

Found, in air-dried salt: loss in a vacuum = 11·8.

$C_{29}H_{40}O_4N_2,2C_2H_2O_4,5H_2O$ (750·6) requires H_2O = 12·0 per cent.

Found, in salt dried in a vacuum: C = 59·8, 60·1; H = 7·0, 6·8.

$C_{29}H_{40}O_4N_2,2C_2H_2O_4$ (660·5) requires C = 60·0; H = 6·7 per cent.

The specific rotatory power was determined in aqueous solution:

$\alpha_D + 0·25°$; $c = 8·019$; $l = 2$-dcm.; $[\alpha]_D + 1·6°$.
$\alpha_D + 0·50°$; $c = 3·856$; $l = 2$-dcm.; $[\alpha]_D + 6·5°$.
$\alpha_D + 0·50°$; $c = 2·958$; $l = 2$-dcm.; $[\alpha]_D + 8·5°$.
$\alpha_D + 0·33°$; $c = 1·454$; $l = 2$-dcm.; $[\alpha]_D + 11·3°$.

Methylation of iso*Cephaeline. Formation of* iso*Emetine.*

0·4 Gram of *iso*cephaeline (T., 1914, **105**, 1626) was dissolved in a solution of 0·05 gram of sodium in 35 c.c. of fusel oil boiling at 130—133°; 0·2 gram of anhydrous sodium methyl sulphate was added, and the mixture boiled for one and a-half hours under a reflux condenser. After acidifying with hydrochloric acid, the liquor was distilled with steam to remove the fusel oil, and the alkaloids were then regenerated to ether by means of sodium carbonate. The ethereal solution was extracted with dilute aqueous sodium hydroxide, which removed 0·15 gram of unchanged *iso*-cephaeline, evaporated to dryness, and converted into the hydrobromide, when 0·17 gram of crude *iso*emetine hydrobromide was obtained. After recrystallisation from water, this salt formed prismatic needles, having the melting point previously recorded, either alone or mixed with *iso*emetine hydrobromide resulting from

the reduction of methylpsychotrine. For further identification, the base was regenerated from the hydrobromide, when it crystallised from ether in the characteristic disks, melting at 97—98° (corr.), both alone and when mixed with a specimen of the base resulting from the reduction of methylpsychotrine.

Methylation of iso*Emetine. Formation of* N-*Methyl*iso*emetine and Isolation of Benzoyl*iso*emetine.*

*iso*Emetine was methylated by methyl sulphate and sodium methoxide, the resulting mixture of *N*-methyl*iso*emetine and unchanged *iso*emetine being separated by removing the latter as the benzoyl derivative, the hydrochloride of which can be extracted from aqueous solution by chloroform. The method is precisely similar to that employed for the methylation of emetine (T., 1914, **105**, 1617), to which reference may be made for further details.

*iso*Emetine, regenerated from 7·2 grams of the hydrated hydrobromide, was dissolved in a solution of 0·5 gram of sodium in 25 c.c. of methyl alcohol and treated with 2·5 grams of methyl sulphate, when 1·3 grams of *N*-methyl*iso*emetine and 2·1 grams of benzoyl*iso*emetine were obtained.

N-*Methyl*iso*emetine* crystallises from ether in clear, colourless, square tablets with bevelled edges. It melts at 152—153° (corr.), and crystallises again on cooling. It suffers no loss in a vacuum.

Found: C = 72·8; H = 8·5.

$C_{30}H_{42}O_4N_2$ (494·5) requires C = 72·9; H = 8·6 per cent.

The specific rotatory power was determined in chloroform solution:

$\alpha_D - 2·55°$; $c = 2·550$; $l = 2$-dcm.; $[\alpha]_D - 50·0°$.

Benzoyl*iso*emetine proved to be identical with the substance previously described under this name (T., 1917, **111**, 439). It formed colourless prismatic needles from acetone, which melted at 207—208° (corr.) alone or when mixed with the preparation to which reference has been made. The specific rotatory power in chloroform solution was found to be $[\alpha]_D + 47·3°$ ($c = 2·833$).

Methylation of N-*Methyl*iso*cephaeline. Formation of* N-*Methyl*iso*emetine.*

The isomeride (T., 1914, **107**, 1624) of *N*-methylcephaeline yields *N*-methyl*iso*emetine on methylation, and is therefore *N*-methyl*iso*cephaeline.

Two grams of the pure isomeride, melting at 196—197° (corr.), were dissolved in a solution of 0·5 gram of sodium in 50 c.c. of

fusel oil, boiling at 130—133°, and boiled for two hours under a reflux condenser with 1·25 grams of anhydrous sodium methyl sulphate. On working up the product in the usual way (compare, for instance, T., 1914, **107**, 1623), 1·4 grams of the phenolic base were recovered, and 0·23 gram of *N*-methyl*iso*emetine was obtained. This base melted at 152—153° (corr.) alone or when mixed with the methylation product of *iso*emetine; the specific rotatory power in chloroform solution was found to be $[\alpha]_D$ −47·6° (c=1·125).

N-*Methyl*iso*emetine Methiodide*.

Twenty-five grams of *iso*emetine hydrobromide were dissolved in 625 c.c. of hot water, cooled, mixed with 50 c.c. of methyl iodide and 25 grams of anhydrous sodium carbonate, and heated on the water-bath. After one and three-quarter hours, the insoluble matter, which was viscous and amorphous at first, had become crystalline, and was collected. It amounted to 21·3 grams, and formed colourless, well-defined, oblong prisms which melted at 290—292° (corr.) after drying at 100°. This salt is very sparingly soluble in cold water.

Found, in air-dried salt, loss in a vacuum = 2·4; in dried salt, I = 32·4.

$C_{32}H_{48}O_4N_2I_2,H_2O$ (796·4) requires H_2O = 2·3 per cent.

$C_{32}O_{48}O_4N_2I_2$ (778·4) requires I = 32·6 per cent.

The specific rotatory power of the hydrated salt was determined in aqueous solution:

α_D + 0·6°; c = 0·324; l = 2-dcm.; $[\alpha]_D$ + 92·6°.

The mother liquors from the crystalline methiodide were concentrated, and deposited 6·5 grams of pale orange-brown resin, which became quite hard, but was not obtained in a crystalline form. The crystalline and amorphous salts were found to give the methine in approximately equal yield.

N-*Methyl*iso*emetinemethine*, $C_{32}H_{46}O_4N_2$.

29·2 Grams of *iso*emetine hydrobromide were converted into methyl*iso*emetine methiodide by the method described above, and the combined crystalline and amorphous methiodides were converted into the anhydro-base by the method employed for methylemetinemethine (T., 1917, **111**, 445). The crude methine was neutralised with 20 per cent. aqueous oxalic acid, and gave 21·1 grams of neutral oxalate in several crops, that is, 75·4 per cent. of the theoretical yield.

*Methyl*iso*emetinemethine oxalate* crystallises from water in

colourless prisms of an elongated diamond shape which are very easily soluble in water. The air-dried salt contains $4H_2O$ and melts at 122—127° (corr.); after drying at 100°, the salt melts at 133—134° (corr.).

Found, in air-dried salt: $H_2O = 10{\cdot}8$, $10{\cdot}7$.

$C_{32}H_{46}O_4N_2,C_2H_2O_4,4H_2O$ (684·6) requires $H_2O = 10{\cdot}5$ per cent.

Found, in air-dried salt: C = 66·4, 66·4, 66·5, 66·5; H = 7·9, 7·9, 7·9, 7·9.

$C_{32}H_{46}O_4N_2,C_2H_2O_4$ (612·6) requires C = 66·6; H = 7·9 per cent.

The specific rotatory power of this salt was determined in aqueous solution:

$$\alpha_D + 0{\cdot}35°;\ c = 4{\cdot}153;\ l = 2\text{-dcm.};\ [\alpha]_D + 4{\cdot}2°.$$

*Methyl*iso*emetinemethine methiodide* separates as a crystalline powder when a concentrated ethereal solution of the methine, prepared by regeneration from the pure oxalate, is warmed with methyl iodide. The salt, so prepared, began to sinter at 155° and effervesced at 163° (corr.); when moistened with cold water, it first became gummy and then crystallised; it appeared to contain methyl iodide of crystallisation, for when it was added to boiling water effervescence took place, and an odour of methyl iodide was observed. The hot aqueous solution deposited the salt on cooling in silky needles, which melt at 178° (corr.) after drying at 100°, and effervesce at about 180°.

Found, in air-dried salt: loss at 110° = 4·0.

$C_{34}H_{52}O_4N_2I_2,2H_2O$ (842·4) requires $H_2O = 4{\cdot}3$ per cent.

Found, in dried salt: I = 31·6.

$C_{34}H_{52}O_4N_2I_2$ (806·4) requires I = 31·5 per cent.

Oxidation of iso*Emetine. Formation of Methylpsychotrine and Rubremetine.*

(1) *With One Molecular Proportion of Iodine.*—This oxidation was carried out essentially in the same way as that of emetine (T., 1917, **111**, 434), but the isolation of methylpsychotrine as hydrogen oxalate was complicated by the fact that *iso*emetine hydrogen oxalate also crystallises from moist alcohol, whereas emetine hydrogen oxalate does not.

Twenty grams of *iso*emetine hydrobromide were recrystallised from 50 c.c. of water, when 19 grams separated. After removing this, the mother liquor gave further small crops of the same salt on concentration, and eventually a liquor which no longer deposited crystals. This was shaken with aqueous sodium hydroxide and ether, and the regenerated base, amounting to 0·04 gram, was con-

verted into the hydrogen oxalate in alcoholic solution, when 0·02 gram of colourless, somewhat spongy crystals was obtained, which, after drying at 100°, sintered at 145°, and gradually melted up to about 200°. The melting point indicates that this hydrogen oxalate did not consist wholly of methylpsychotrine hydrogen oxalate, whence the original hydrobromide contained less than 1 per cent. of methylpsychotrine.

Nine grams (part of the 19 grams) of purified *iso*emetine hydrobromide were then converted into the base and oxidised with 3·2 grams of iodine in 80 c.c. of absolute alcohol by heating for three and a-half hours at 100°.

The product was mixed with dilute sulphurous acid, evaporated to about half its volume, mixed with aqueous sodium hydroxide, and extracted with chloroform. The chloroform extract was completely extracted with dilute hydrochloric acid, dried, and distilled, when it left 2·3 grams of dark brown resin. This was extracted with small quantities of boiling water, and the filtered extracts were mixed with a small quantity of aqueous potassium iodide, when 0·9 gram of rubremetine hydriodide separated in minute red needles, which, after drying at 100°, began to melt at 177° (corr.) either alone or when mixed with rubremetine hydriodide prepared by the oxidation of emetine. The identification of the salt with rubremetine hydriodide was further confirmed by analysis. (Found, in air-dried salt, $H_2O = 13·5$; in dried salt, I = 21·3. Calc.: $H_2O = 13·0$; I = 21·2 per cent.)

The hydrochloric acid extract of the chloroform extract was mixed with aqueous sodium hydroxide and extracted with chloroform. The chloroform residue was converted into the hydrobromide, when 5·0 grams of *iso*emetine hydrobromide were recovered. The mother liquors, shaken with aqueous sodium hydroxide and ether, gave 0·7 gram of base, which was dissolved in alcohol containing 0·4 gram of hydrated oxalic acid. On inoculating with methylpsychotrine hydrogen oxalate, 0·13 gram of nearly colourless crystals, melting at 140—145° (corr.), separated. For purification, the base was regenerated from this material and again converted into hydrogen oxalate, when 0·08 gram was obtained, which melted at 145—150° (corr.), methylpsychotrine hydrogen oxalate melting at 150—155° (corr.) in the same bath, and a mixture of the two substances intermediately. The aqueous solution of the salt showed the blue fluorescence characteristic of methylpsychotrine salts. A determination of the specific rotatory power gave a low value, $[\alpha]_D + 33°$ ($c = 1$), and consequently further evidence of the identity of the substance was required. Accordingly, the base was regenerated, neutralised with dilute sulphuric

acid, and the solution evaporated to dryness, then moistened with absolute alcohol and evaporated to dryness several times. Finally, it was dissolved in a few drops of absolute alcohol and inoculated with methylpsychotrine sulphate monohydrate, when a colourless, crystalline powder separated, which melted at 245° (corr.), methylpsychotrine sulphate melting at 248° (corr.), and a mixture of the two substances at 246° in the same bath.

(2) *With Ferric Chloride.*—Two grams of *iso*emetine hydrochloride were oxidised with an aqueous solution of 40 grams of commercial hydrated ferric chloride, the details of manipulation being the same as previously described for the oxidation of emetine with ferric chloride (T., 1914, **105**, 1627). After crystallisation from water, 0·45 gram of crude rubremetine hydrochloride was obtained. This was purified in the manner previously described, and identified by comparison with a specimen prepared from emetine.

Action of Sodium Amyloxide on iso*Emetine.*

The base liberated from 3 grams of *iso*emetine hydrobromide was dissolved in a solution of 1·0 gram of sodium in 50 c.c. of fusel oil (b. p. 130—133°), and boiled for fourteen hours under a reflux condenser. After the addition of 6 c.c. of hydrochloric acid and 20 c.c. of water, the fusel oil was removed by steam distillation, and the non-phenolic and phenolic bases were recovered and separated in the usual way. The latter—amounting to 0·3 gram of yellow resin—were neglected, whilst the non-phenolic bases were found to consist almost entirely of *iso*emetine, for when treated with hydrobromic acid they gave 2·3 grams of pure *iso*emetine hydrobromide, the mother liquors containing only a trace of material.

Emetine, when treated in a similar manner, was also mainly recovered unchanged, except in so far as it had become hydrolysed, and no evidence of the formation of *iso*emetine could be obtained.

Preparation and Separation of α- and β-N-Methylemetine Methiodides.

Ten grams of emetine hydrobromide were dissolved in 250 c.c. of hot water, and the solution, after cooling to some extent, was mixed with 20 c.c. of methyl iodide and 10 grams of anhydrous sodium carbonate. It was then heated on the water-bath under a reflux condenser so that the methyl iodide boiled. After three hours crystals began to form, and gradually increased in quantity; after boiling for a fourth hour, the excess of methyl iodide was

removed by distillation and the liquor filtered from the first crop of crystals—8·0 grams; m. p. 210—220°; $[\alpha]_D$ −6°. On cooling, the mother liquor deposited a second crop of crystals—2·6 grams; m. p. 220—260°; $[\alpha]_D$ +32·4°—whilst a third fraction was obtained by extraction with chloroform as a nearly colourless resin (0·7 gram) which deposited crystals after solution in water. After recrystallising the first crop from water twice, the previously known α-methiodide was obtained in a pure state; it had the melting point previously recorded, namely, 225—226° (corr.), and formed prisms containing between 3 and $4H_2O$. (Found: H_2O=7·9. Calc. for $3H_2O$, 6·3; for $4H_2O$, 8·5 per cent.) The specific rotatory power was determined in aqueous solution:

$$\alpha_D -0{\cdot}23°;\ c=1{\cdot}145;\ l=2\text{-dcm.};\ [\alpha]_D -10{\cdot}0°.$$

After prolonged fractional crystallisation, there were obtained 5·35 grams of this salt in a pure state, 2·6 grams less pure, melting at 210—220°, various small crops melting between 220° and 260°, and 0·45 gram of the pure *β-methiodide*.

α-N-Methylemetine methochloride was prepared from the α-methiodide by double decomposition with silver chloride, concentration of the filtered solution to a syrup, and precipitation with acetone, when it formed small, colourless needles which melted at 133° (corr.) after drying at 100°, and at 200° (corr.) after drying at 110°.

Found, in air-dried salt: loss at 100—110°=15·2.

$C_{32}H_{48}O_4N_2Cl_2,6H_2O$ (703·6) requires H_2O=15·3 per cent.

Found, in salt dried at 100—110°: C=64·2, 64·2; H=8·1, 8·0.

$C_{32}H_{48}O_4N_2Cl_2$ (595·5) requires C=64·5; H=8·1 per cent.

The specific rotatory power of this salt was determined in aqueous solution:

$$\alpha_D -0{\cdot}18;\ c=3{\cdot}986;\ l=2\text{-dcm.};\ [\alpha]_D -2{\cdot}3°.$$
$$\alpha_D -0{\cdot}18;\ c=1{\cdot}993;\ l=2\text{-dcm.};\ [\alpha]_D -4{\cdot}5°.$$

β-N-Methylemetine methiodide forms long, flat plates from water, which melt at 262° (corr.) after drying at 100°. Like the α-salt, it is easily soluble in hot, but very sparingly so in cold water.

Found, in air-dried salt: H_2O=5·2.

$C_{32}H_{48}O_4N_2I_2,2\frac{1}{2}H_2O$ (823·4) requires H_2O=5·5 per cent.

Found, in salt dried in a vacuum: C=49·6; H=6·3.

$C_{32}H_{48}O_4N_2I_2$ (778·4) requires C=49·3; H=6·2 per cent.

The specific rotatory power was determined in aqueous solution:

$$\alpha_D +1{\cdot}15°;\ c=0{\cdot}844;\ l=2\text{-dcm.};\ [\alpha]_D +68{\cdot}1°.$$

Formation of N-*Methylemetinemethine from the β-Methiodide.*

0·5 Gram of the β-methiodide was converted into the methine by the method used for the α-methiodide (T., 1917, **111**, 445). The crude tertiary base, extracted by ether (0·27 gram), was dissolved in alcohol and neutralised with oxalic acid, when 0·12 gram of methylemetinemethine oxalate crystallised in prisms. It melted at 82—83° (corr.), a mixture with the salt prepared from the α-methiodide melting at the same temperature.

For further identification, the water of crystallisation was estimated (Found: $H_2O=18·9$. Calc.: $H_2O=18·1$ per cent.), and an approximate determination of the specific rotatory power was made [Found: $[\alpha]_D$ −19·5° ($c=1·2$ in water); previously found for salt from α-methiodide, $[\alpha]_D$ −24·6]. It was also observed that the methine from the β-methiodide gave a hydrochloride, which crystallised from absolute alcohol in plates. A similar salt had previously been obtained from the methine prepared from the α-methiodide, by the following method.

N-*Methylemetinemethine Hydrochloride.*

A quantity of the base, regenerated from the pure oxalate to ether, was dissolved in dilute hydrochloric acid and evaporated to dryness. It was next dissolved in absolute alcohol and evaporated to dryness, this operation being repeated several times. It was then dissolved in a small volume of absolute alcohol, when it separated in colourless, quadrilateral plates, which melted at 236° (corr.) after drying at 100°. This salt is very easily soluble in water.

Found, in air-dried salt: loss at 105° = 2·4, 3·7.

$C_{32}H_{46}O_4N_2,2HCl,H_2O$ (613·4) requires $H_2O=2·9$ per cent.

Found, in salt dried at 105°: Cl = 11·5, 11·5.

$C_{32}H_{46}O_4N_2,2HCl$ (595·5) requires Cl = 11·9 per cent.

In conclusion, my thanks are due to Mr. E. C. S. Jones for assistance in this investigation.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.1. [*Received, February* 28th, 1918.]

XXVII.—*The Supposed Formation of Ergotoxine Ethyl Ester from Ergotinine. A Correction.*

By George Barger and Arthur James Ewins.

Some years ago (T., 1910, **97**, 284) we obtained a crystalline phosphate by boiling ergotinine in alcoholic solution with phosphoric acid, and we concluded that the salt was the phosphate of ergotoxine ethyl ester. This is not so; it is the phosphate of ergotoxine itself. Ergotoxine, $C_{35}H_{41}O_6N_5$, is the hydrate of ergotoxine, $C_{35}H_{39}O_5N_5$ (Barger and Carr, T., 1907, **91**, 337), and at the time of our previous work the phosphate of ergotoxine (the first salt to be crystallised) had been obtained exclusively in the form of fine needles (T., 1910, **97**, 286, Fig. 2), whilst our supposed ester salt crystallised in broad plates (*loc. cit.*, Fig. 1). Similar differences of crystalline form were observed in the hydrochlorides (*loc. cit.*, Figs. 3 and 4), and oxalates, prepared from the two phosphates. (On the other hand, each pair of salts had approximately the same melting point.) We chiefly relied, however, on an analysis (1 per cent. more carbon than in ergotoxine phosphate, as calculated) and a Zeisel determination of the ethoxy-group. (Found, 5·97. Calc., 5·82 per cent.)

Some years later, Mr. F. H. Carr and Dr. F. L. Pyman determined the methoxy- and methylimino-groups in ergotoxine and in ergotinine, and drew the conclusion that both alkaloids contain one *O*-methyl and one *N*-methyl group. In that case we ought to have found two alkyloxy-groups in the ester, as Messrs. Carr and Pyman pointed out to us. Their determinations were as follows:

Ergotinine.—The substance was of good colour and crystalline appearance, and melted at 231°. It suffered no appreciable loss on drying even at 130°.

1. 0·4051 gave 0·1241 AgI below 180°. OMe = 4·0.
   and 0·1004 AgI above 290°. NMe = 3·1.
2. 0·3019 gave 0·0851 AgI below 180°. OMe = 3·7.
   and 0·0942 AgI above 290°. NMe = 3·9.

3. After a blank distillation of the hydriodic acid yielding 0·0053 AgI:

0·1457 gave 0·0258 AgI below 180°. OMe = 2·3.

4. After a blank distillation of the hydriodic acid yielding 0·0123 AgI:

0·4128 gave 0·0794 AgI below 180°. OMe = 2·5.
and 0·1139 AgI above 290°. NMe = 3·4.

5. After a blank distillation of the hydriodic acid (10 c.c.) yielding 0·0098 AgI and the subsequent addition of 5 c.c. of acetic anhydride:

0·4127 gave 0·1548 AgI below 180°. OMe = 4·9.
and 0·0688 AgI above 290°. NMe = 2·1.

6. After a blank distillation of the hydriodic acid (10 c.c.) yielding 0·0218 AgI, and the subsequent addition of 5 c.c. of acetic anhydride:

0·4130 gave 0·1401 AgI below 180°. OMe = 4·5.
and 0·0764 AgI above 290°. NMe = 2·3.

7. Blank distillation with 10 c.c. of hydriodic acid for one hour gave 0·0027 AgI, after addition of 5 c.c. of acetic anhydride, and a double distillation for two hours gave 0·0183 AgI, after a further double distillation for two and one-third hours gave 0·0025 AgI:

0·4966 gave 0·1501 AgI below 180°. OMe = 4·0.
and 0·0713 AgI above 290°. NMe = 1·7.
$C_{35}H_{39}O_5N_5$ requires OMe = 5·1; NMe = 4·8 per cent.

Ergotoxine Phosphate.—

1. 0·3976 gave 0·1204 AgI at 140—195°. OMe = 4·0.
2. 0·3926 „ 0·1614 AgI „ 140—195°. OMe = 5·4.
3. 0·2302 „ 0·0732 AgI „ 140—195°. OMe = 4·2.
4. 0·3954 gave 0·1055 AgI below 180°. OMe = 3·5.
and 0·0663 AgI above 290°. NMe = 2·1.
5. 0·3914 gave 0·0982 AgI below 180°. OMe = 3·3.
and 0·0678 AgI above 290°. NMe = 2·0.
6. 0·1420 gave 0·0494 AgI below 180°. OMe = 4·6.
and 0·0364 AgI above 290°. NMe = 3·2.

Specimen No. 1 was prepared from ergotinine, the rest from ergot. Nos. 4–6 were dried at 100° and analysed with the addition of acetic anhydride. The melting point was 187—188°.

0·1482, dried at 100° (mixed with CuO), gave 0·3120 CO_2 and 0·0900 H_2O. C = 57·4; H = 6·8.
$C_{35}H_{41}O_6N_5,H_3PO_4$ requires C = 57·9; H = 6·1; OMe = 4·3; NMe = 4·0 per cent.

On receipt of the above data we re-examined the action of alcoholic phosphoric acid on ergotinine, on a larger scale than was originally possible. We were able to transform the salt, first obtained as needles, into plates by recrystallisation from alcohol.

One gram of ergotinine was suspended in 15 c.c. of absolute alcohol, and rather more than one molecular proportion of syrupy phosphoric acid was added. On heating under reflux on the water-

bath the ergotinine dissolved, but after a total heating of thirty to forty-five minutes the solution became almost solid with a mass of prismatic needles, which were collected.

The yield was 0·95 gram, or 80 per cent. of the theoretical; the melting point, 189—190°. After drying at 100°:

0·5720 gave 0·0246 AgI (two hours at 140—150°). OMe=0·56.

On recrystallisation from alcohol, plates were formed, melting at 190°, which were analysed:

0·4216 gave 0·0412 AgI (two hours at 150°). OMe=1·3.

From these experiments we conclude that the phosphate was that of ergotoxine, and that no ethyl ester grouping was present, for it would have been readily removed under the analytical conditions employed.

We next examined the action of hydriodic acid on ergotinine, using in each case 10 c.c. of acid (D 1·7) and 5 c.c. of acetic anhydride, the bath being heated for two hours at the temperature intervals indicated.

A. Ergotinine, older (less pure) specimen:

0·4127 gave 0·1259 AgI at 150—195° and 0·0389 AgI at 340—350°. Total AgI=0·1648. OMe=5·3 *or* NMe=4·9.

B. Ergotinine, purer specimen:

0·4129 gave 0·0105 AgI at 140—145°, 0·1333 AgI at 180—200°, and 0·0303 AgI at 300—370°. Total AgI=0·1741. OMe=5·6 *or* NMe=5·2.

$C_{35}H_{39}O_5N_5$ requires OMe=5·1; NMe=4·8 per cent.

We have calculated our results from the total silver iodide formed, for we believe that only one methyl group is present, and think that this methyl group is attached to nitrogen. Messrs. Carr and Pyman's six analyses, in which heating was continued to 290°, when calculated as NMe only, give the mean 6·4 per cent., which is one-third more than the theoretical. In our opinion the amount of silver iodide is, however, insufficient to account for a methoxy- as well as a methylimino-group. There is abundant evidence that many methylimino-groups give off part of their methyl as methyl iodide on merely boiling with hydriodic acid, particularly if carbonyl groups are adjacent (Busch, *Ber.*, 1902, **35**, 1565; Goldschmiedt and Hönigschmid, *Ber.*, 1903, **36**, 1850; *Monatsh.*, 1906, **27**, 849; Kirpal, *Ber.*, 1908, **41**, 819). Decker (*Ber.*, 1903, **36**, 2895) has pointed out that in this way *N*-alkyl may be mistaken for *O*-alkyl, and Herzig (*Monatsh.*, 1908, **29**, 295) states that with nitrogenous substances, unless the formation of silver iodide begins soon after the hydriodic acid boils, and proceeds rapidly to an end, it is unsafe to conclude that a methoxyl group is present. In

our own experiments the evolution of methyl iodide from the boiling acid was slow and incomplete, whence our conclusion, that ergotinine and ergotoxine contain one *N*-methyl group, but no methoxy-group.

We desire to thank Messrs. Carr and Pyman for having directed our attention to the error in our former paper, and for having placed their analytical results at our disposal.

LISTER INSTITUTE OF PREVENTIVE MEDICINE,
CHELSEA GARDENS, LONDON, S.W. [*Received, March 16th*, 1918.]

XXVIII.—*Interaction of Formaldehyde and Carbamide.*

By AUGUSTUS EDWARD DIXON.

IN a paper by Dixon and Taylor on the interaction of aldehydes and thiocarbamides (T., 1916, **109**, 1244), it is mentioned in passing that a molecular mixture of carbamide and formaldehyde, when condensed by means of hydrochloric acid, yielded a substance, apparently identical with the methylenecarbamide obtained by Hemmelmayr (*Monatsh.*, 1891, **12**, 94), from carbamide and chloromethyl alcohol. Subsequently—but not until most of the present investigation had been completed—it was learned that several chemists have already studied the interaction between carbamide and formaldehyde (see, for example, Hoelzer, *Ber.*, 1884, **17**, 659; Tollens, *ibid.*, 1896, **29**, 275; Goldschmidt, *ibid.*, 2439; *Chem. Zeit.*, 1897, **21**, 460, 586; Einhorn and Hamburger, *Ber.*, 1908, **41**, 24). In one case only is it necessary to comment on the results.

According to Goldschmidt, carbamide yields, with "excess" of formaldehyde, a compound, $C_5H_{10}O_3N_4$ (that is, $2CH_4ON_2 + 3CH_2O - 2H_2O$), which is formed alike in the presence or in the absence of acids*; and as the yield is theoretical, he concludes that carbamide may thus be determined quantitatively. With these statements, the author's experience does not quite tally; for, in an acidified mixture, the precipitate may not be formed quantitatively; it may have a different composition, or it may not be formed at all. Moreover, in a neutral mixture of the components, even after six months' keeping, no sign of condensation was observed (Expt. 1).

From a slightly acidified solution of carbamide (1 mol.), the condensate, with 0·75 mol. of formaldehyde, is methylenecarbamide;

* Presumably, this means in a neutral solution

with 1 mol. of formaldehyde it is slightly contaminated with Goldschmidt's compound. With $1\frac{1}{2}$ mols. of formaldehyde, and thenceforward up to well beyond 2 mols., the latter compound is the sole product. Further increase of the formaldehyde ratio diminishes the yield, which, at 4 mols., is small, the product being a substance, $C_5H_{12}O_4N_4$; whilst, with 11 mols., condensation ceases.

The precipitates obtained by "catalysing" solutions of carbamide containing variable proportions of formaldehyde, although differing, it may be, largely in composition, exhibit a close general resemblance. They occur in minute, white granules, apparently amorphous, each of which, in plane-polarised light, usually displays a black cross, like that of certain starches. Practically insoluble in all the common solvents, and in cold, dilute mineral acids, they are resolved by heating with the latter into formaldehyde and carbamide; infusible, they decompose at a high temperature, considerably variable with the duration of the preliminary heating (somewhere in the neighbourhood of 240—250°, uncorr.).

From these facts it is concluded that the so-called methylenecarbamide cannot properly be represented by the simple formula, $CO<^{NH}_{NH}>CH_2$, but is a dimeride, containing, like Goldschmidt's compound, two carbamide residues in the molecule. Its configuration may be represented as $CO<^{NH\cdot CH_2\cdot NH}_{NH\cdot CH_2\cdot NH}>CO$ (I), Goldschmidt's compound being the methylol derivative,

$$CO<^{NH\text{———}CH_2\cdot NH}_{N(CH_2\cdot OH)\cdot CH_2\cdot NH}>CO \text{ (II)},$$

whilst the substance, $C_5H_{12}O_4N_4$, mentioned above, is probably similar, that is, $CO<^{NH\text{———}CH_2\text{———}NH}_{NH\cdot CH_2\cdot OH\ \ HO\cdot CH_2\cdot NH}>CO$ (III). The formula, $CO(NMe\cdot CO\cdot NH_2)_2$, proposed by Goldschmidt (*loc. pr. cit.*) for his compound does not seem to be in harmony with its decomposition into carbamide and formaldehyde by dilute acids; it is slowly attacked, too, by hot alkalis, with the evolution of ammonia, but no methylamine was detected.

Ready-formed "methylenecarbamide," when kept in contact with formalin, did not combine with it, to yield the compound II above, nor did this, under like conditions, give the possible derivative, $CO<^{N(CH_2\cdot OH)\cdot CH_2\cdot NH}_{NH\cdot CH_2\cdot(CH_2\cdot OH)N}>CO$ (IV); the last compound, in fact, has not been isolated, even in circumstances apparently favourable.

From a neutral solution of carbamide (1 mol.) in formalin (1 mol.), methylolcarbamide, together with a little dimethylolcarbamide, is deposited on concentration in a vacuum over sulphuric acid. The former compound, it would seem, is a near precursor of

"methylenecarbamide"; for, such a solution, if kept for one-and-a-half hours, so as to give the components a little time to combine before treatment with acid (they do not quickly unite in quantitative amount), began to condense nearly twice as soon as a mixture, otherwise similar, but freshly prepared. Moreover, when ready-formed methylolcarbamide, in like circumstances of concentration and of temperature, was acidified to the same extent, condensation started in one-fifteenth of the time required by a freshly-made mixture of carbamide and formaldehyde (Expt. 15). Dimethylolcarbamide, on the other hand, is relatively slow to condense—a fact already noted by Einhorn and Hamburger (*loc. cit.*). The reason, no doubt, is that the dimethylol derivative of 'methylenecarbamide' (IV, above) resists formation in the presence of acids; so that, until time enough has passed for the elimination of a certain amount of formaldehyde, condensation is barred. No doubt, too, the complete stoppage of the carbamide–formaldehyde condensation (see above) by a very large excess of formaldehyde is due to the maintenance of the carbamide in the state of its dimethylol derivative; if the uncondensable mixture is added to a concentrated aqueous solution of carbamide, a precipitate separates forthwith (Expt. 9).

Having regard to the above facts, one may reasonably judge that "methylenecarbamide" results from the decomposition of some compound, generated by the action of, say, hydrochloric acid on methylolcarbamide. Of the stages that must occur, the first is probably the change of $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OH$ into

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Cl,$$

a compound, likely to be unstable, owing to the loss (at least, if water is present) of hydrogen chloride. Through the elimination of hydrogen chloride there originates the residue, $\cdot NH{\cdot}CO{\cdot}NH{\cdot}CH_2\cdot$, whence, by polymerisation, the compound $CO\langle{}^{NH\cdot CH_2\cdot NH}_{NH\cdot CH_2\cdot NH}\rangle CO$ ("methylenecarbamide") could occur. An essentially similar change, in fact, has been observed by Chattaway (T., 1909, **95**, 236), chlorocarbamide, by the loss of hydrogen chloride, polymerising thus:

$$CO\langle{}^{NH_2}_{NHCl} + CO\langle{}^{NHCl}_{NH_2} \rightarrow 2HCl + CO\langle{}^{NH\cdot NH}_{NH\cdot NH}\rangle CO.$$

Really, however, the carbamide–formaldehyde process is somewhat more complex than is here indicated, for, as previously mentioned, molecular proportions of carbamide and formaldehyde do not give pure "methylenecarbamide"; moreover, the condensate of a tolerably pure specimen of methylolcarbamide was markedly contaminated with a substance poorer in nitrogen. Further inquiry

showed that, in the acid condensation of methylolcarbamide, a secondary reaction occurs, the compound being decomposed, to some extent, into carbamide and formaldehyde (a change like that of aldehyde-ammonia, except that the acid completely neutralises the ammonia, whereas it has but little power to fix a base so feeble as carbamide).

Now, an aqueous solution of methylolcarbamide gives, with sodium nitroprusside and phenylhydrazine, no reaction for formaldehyde, nor does it show the reaction for carbamide with mercuric nitrate; neither, when once formed, does "methylenecarbamide" unite with formaldehyde. As the last-named is produced immediately—that is, prior to condensation—the inference was that it must attack the nascent methylenecarbamide residues. If so, and if the proportion of formaldehyde is not sufficient to produce the incondensable dimethylol residues alone, one could foresee that methylolcarbamide, when condensed in the presence of a suitable amount of formaldehyde, should furnish Goldschmidt's compound. On experiment with molecular proportions of the two, this forecast was verified (Expt. 13).

As regards the condensation of carbamide with formaldehyde, a like mechanism is imaginable, since, even in the presence of an acid, the organic components might conceivably unite to form methylolcarbamide. With mixtures only slightly acidified, and hence condensing but slowly, this may be the case; on the other hand, with freely acidified mixtures, the condensation of which may happen within a few seconds, the action must run a different course. Experiment, in fact, has shown that condensation can be accomplished in circumstances where the existence of methylolcarbamide is precluded.

Thus, if carbamide (1 mol.) is dissolved in formalin (1 mol.) previously saturated with hydrogen chloride (and so changed into chloromethyl alcohol), no precipitate appears, a clear syrup being formed instead. If hydrogen chloride is passed through a molecular solution of carbamide in formalin until the clot which first separates dissolves again, a clear syrup is formed, as before. Finally, if hydrogen chloride is led over moist, ready-formed "methylenecarbamide" (or if the latter is added to fuming hydrochloric acid), the solid disappears, giving place to a syrup. Each of these syrups, when poured into water, yields instantly a voluminous, white precipitate of the condensation product. On prolonged exposure in a vacuum over lime and over sulphuric acid, a clear, odourless, resinous material is left; deliquescent, evolving with cold sulphuric acid fumes of hydrogen chloride, and decomposed at once by water, the whole of the contained halogen passing

into solution as hydrochloric acid, whilst a condensation product is deposited.

These changes, perhaps, may be represented by the equations:

(*a*) $CO(NH_2)_2 + CH_2Cl{\cdot}OH \longrightarrow H_2O + NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Cl$,

(*b*) $CO\begin{matrix}<^{NH}_{NH}>\end{matrix}CH_2 + HCl \longrightarrow NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Cl$,

the product, with excess of water, decomposing as earlier suggested (in the latter equation, for simplicity, the halved formula is used for "methylenecarbamide"). The substances, however, were not pure, nor, by reason of their deliquescence and instability, could any method be devised for their purification.

The possibility that water, in removing the elements of hydrogen chloride, might produce methylolcarbamide (which, of course, would react with the liberated acid), was negatived by the observation that the change occurred equally when the material was added to dilute alkali hydroxide or to a solution of ammonia. Had methylolcarbamide thus been formed, the acid simultaneously being neutralised, no immediate condensation would have followed; although not decisive, these results are consistent with the view already suggested, namely, that "methylenecarbamide" originates from a residue, $\cdot NH{\cdot}CO{\cdot}NH{\cdot}CH_2\cdot$, derived from the compound, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Cl$, or from one of its congeners; that is, in the acid process, with which alone the present paper is concerned.

Dimethylolcarbamide may be produced by evaporating a neutral solution of carbamide in a sufficiency of formalin and crystallising the solid residue from alcohol. The fused material soon decomposes into water, formaldehyde and Goldschmidt's compound, $C_5H_{10}O_3N_4$, an aqueous solution, when acidified, behaving in the same way.

From random acidified mixtures of carbamide and formaldehyde, $C_5H_{10}O_3N_4$ is the product likely to preponderate. The result, however, depends on the conditions imposed; and that different workers, handling these ill-defined, amorphous, insoluble, and generally similar materials should have disagreed, more or less, as to the outcome, is not surprising. In the present research, the results to some extent have been disentangled; it is almost certain, however, that the condensation of carbamide with formaldehyde is a reaction more complex than has been indicated above, both as regards the mechanism and the composition of the products of condensation. It need scarcely be added that, in these reactions, hydrochloric acid is no more a catalyst than is the water or the carbamide or the formaldehyde.

Any definite acid that does not itself decompose carbamide may accomplish the foregoing condensations, either with mixtures of

carbamide and formaldehyde or with the methylolcarbamides, but, of the products obtained with nearly a dozen different acids, no quantitative analyses were made. Carbonic acid was the weakest tried; at the ordinary temperature and under the pressure of one atmosphere, a solution of one molecular proportion of carbamide in one of formalin, previously neutralised, remained clear for two or three days, but gave ultimately a dense precipitate. None of the pure condensation products when kept for an hour in contact with water and urease gave a detectable quantity of ammonia.

Experimental.

Unless it is otherwise stated, the "formaldehyde" used in the experiments described below was commercial formalin containing 37·5 grams of formaldehyde in 100 c.c. of the solution.

Expt. 1.—To 6 grams of carbamide in 100 c.c. of water (free from air), 9 c.c. of formalin were added; the mixture, neutralised with dilute sodium hydroxide and sealed up from contact with the external air, remained clear during six months, at the end of which period the experiment was stopped. Portions removed from time to time and acidified with hydrochloric acid or with sulphuric acid became densely turbid within a few seconds.

Expt. 2.—Without the preliminary neutralisation, Expt. 1 was repeated; in four hours, opalescence was visible, and next day a copious precipitate had separated.

Expt. 3.—Expt. 2 was repeated, 2 c.c. of formic acid solution being added to the mixture, which became turbid in less than half an hour. Next day, the precipitate was removed, washed with boiling water, and dried; its weight amounted to 0·91 of that possible for $C_4H_8O_2N_4$. The product consisted of minute, nearly spherical granules showing in plane-polarised light a black cross, and decomposing with effervescence and browning at about 242° (uncorr.) (in another experiment, at 239°). With rapid heating, the temperature of decomposition may rise by at least 10°. (Found: N = 38·3; $C_4H_8O_2N_4$ requires N = 38·89 per cent.)

When the carbamide–formaldehyde ratio was exactly 1:1, the percentage of nitrogen in the condensation product was 38·4, the same result also being obtained when a solution containing only 2 per cent. of carbamide was condensed; in both cases, hydrochloric acid was the catalyst used.

Expt. 4.—Carbamide (1 mol.) in tepid aqueous solution and formaldehyde (0·7 mol.), when condensed with hydrochloric acid, yielded a product similar to the preceding, but giving N = 38·9 per cent.

A quantity kept for twenty-four hours in contact with a large excess of formalin and then analysed contained about 1 per cent. of nitrogen less than before; hence the ready-formed material does not unite with formaldehyde to produce Goldschmidt's compound (N = 32·18 per cent.). The slight diminution in the nitrogen-content is probably due to the presence of a little paraformaldehyde, an insoluble, gelatinous material, which tends to separate from formaldehyde solutions when acidified and exposed to the air. Always, in fact, when the condensing mixtures contain free formaldehyde, a skin of this substance appears on the surface, and has to be removed; but, even so, the nitrogen-content is often a fraction of a per cent. below the calculated value.

Expt. 5.—A solution of carbamide (1 mol.) in its own weight of water, slightly warmed and mixed with formaldehyde (1·5 mols.), was condensed with hydrochloric acid. Time, three seconds; yield, 0·87 of that calculated for $C_5H_{10}O_3N_4$. (Found: N = 31·7; $C_5H_{10}O_3N_4$ requires N = 32·18 per cent.)

Notwithstanding the large diminution in the percentage of nitrogen, the properties and reactions were much the same as those of "methylenecarbamide." The substance was decomposed by boiling, dilute mineral acids into carbamide and formaldehyde; it was insoluble in all the common solvents; the granules showed in plane-polarised light and under a magnification of 600 diameters the black cross exhibited by the compound mentioned.

Expt. 6.—Carbamide (1 mol.), dissolved in formaldehyde (2 mols.) at the ordinary temperature, was condensed with hydrochloric acid. Time, fifteen seconds (five seconds when the mixture was kept for one and a-half hours previously to acidification); yield, about the same as in the last experiment. Properties, similar; decomposing point, 244°, or with rapid heating 254° (uncorr.). (Found: N = 31·6; $C_5H_{10}O_3N_4$ requires N = 32·18 per cent.)

Expt. 7.—Expt. 6 was repeated with formic acid as "catalyst," a little water being added later to prevent dense solidification. Time, about two minutes; yield, 0·75 of the calculated; decomposing point, with moderately slow heating, 240°. (Found: N = 32·1; $C_5H_{10}O_3N_4$ requires N = 32·18 per cent.)

After five days' contact with formalin in excess, found N = 32·2 per cent.; no combination, therefore, had occurred.

Expt. 8.—Carbamide (1 mol.) in formaldehyde (4 mols.) gave with hydrochloric acid a slight turbidity, not increased by dilution with water. Very slowly, the deposit thickened, and after twenty-four hours was removed; its weight was but 0·35 of that (4·5 grams) of the carbamide employed. The decomposing point was

a shade lower than in the preceding cases (about 233° when put into the apparatus at 150° and 243° when put in at 205°); otherwise, the substance had the properties already described. (Found: N = 29·3; $C_5H_{12}O_4N_4$ requires N = 29·17 per cent.)

This material appears to contain 1 mol. of water more than the compound, $C_5H_{10}O_3N_4$, obtained with a smaller amount of formaldehyde. The experiment was repeated, the mixture being allowed to remain for an hour before treatment with the acid; no difference, however, was noticeable in any way, except that, after forty-eight hours, the yield was 0·48 of the weight of carbamide taken, and that some flakes of paraformaldehyde were present. By sifting, these were removed and the nitrogen was estimated; it was almost the same as before, namely, 29·1 per cent. Possibly, the compound has the structure represented by the formula $NH_2{\cdot}CO{\cdot}N(CH_2{\cdot}OH){\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OH$, or the methylol groups may be attached to the terminal nitrogen atoms.

Expt. 9.—With 11 mols. of formaldehyde to 1 mol. of carbamide, although the temperature rose perceptibly on the addition of the acid (hydrochloric), the mixture remained clear. Dilution with water or treatment with more acid had no effect, but after a few days' exposure in an open vessel, some paraformaldehyde began to separate. When the clear liquid was poured into a concentrated solution of carbamide, a condensation product rapidly appeared, of which no analysis was made.

In all the preceding experiments, the amount of hydrochloric acid used was roughly 1 c.c. of the concentrated acid (D 1·16) per 6 grams of carbamide; with much larger proportions of acid, the results were as stated below.

Expt. 10.—Two grams of carbamide, in each case, were dissolved in fuming hydrochloric acid: (i) 1 c.c.; (ii) 2 c.c.; (iii) 3 c.c.; (iv) 4 c.c.; (v) 6 c.c. Then, to each of the first four solutions were added 2·5 c.c. of formalin, diluted with the same acid to 4 c.c.; to the fifth, 3 c.c. of formalin; the respective temperatures attained were 55°, 55°, 52°, 48°, and 44°. Soon, (i) became opaque and solidified; (ii), on cooling, changed to a silica-like jelly; (iii) developed presently a few small clots, which later redissolved; (iv) and (v) remained permanently clear; all the solutions, when diluted with water, forthwith became thickly turbid. After remaining for ten days in a vacuum over lime and sulphuric acid respectively, (iv) formed a stiff, almost solid syrup, giving up to water HCl = 23·5 per cent. of its weight.

Expt. 11.—Hydrogen chloride was passed through a cooled solution of carbamide in 1 molecular proportion of formaldehyde, and the resultant clear, viscous syrup poured off from the clot of con-

densation product. In a vacuum, as before, the syrup, after several weeks, changed to a resin, which decomposed instantly with water, giving up to the latter, HCl = 25·4 per cent. On exposure to the air, the resin first deliquesced, yielding a clear, mobile liquid; as more moisture was absorbed, this became turbid, and finally solidified, owing to the separation of a condensation product. The experiment was repeated, the gas being passed until all the clot had redissolved; the syrup, treated as before, gave a clear resin having the properties described above, and yielding to water HCl = 24·5 per cent.

Expt. 12.—Dry hydrogen chloride had no visible effect on dry "methylenecarbamide," but when the latter was moistened and the passage of the gas continued, the solid gave place to a colourless syrup, gradually hardening in a vacuum. To water, the solid product gave up HCl = 27·3 per cent., a condensate separating, in which was found N = 37·85 per cent. (the sample of "methylenecarbamide" taken for experiment contained N = 38·0 per cent.). When added to dilute alkali hydroxide or to a solution of ammonia, the chloro-derivative behaved exactly as towards water, hydrogen chloride being eliminated and neutralised by the excess of alkali present, whilst a condensation product was instantly deposited.

Like results were obtained when carbamide was dissolved in formalin, previously saturated with hydrogen chloride (or mixed with excess of fuming hydrochloric acid), and when "methylenecarbamide" was dissolved in cold, fuming hydrochloric acid, the product in all cases being a syrup, behaving as described above. From the foregoing results, it is evident that carbamide, formaldehyde, hydrogen chloride, and water together produce a balanced system, the equilibrium of which depends on the concentrations of the various components.

Solid carbamide hydrochloride, when exposed to the fumes obtained by rapidly distilling paraformaldehyde, did not appear to undergo any change.

Methylolcarbamide.

The somewhat elaborate procedure recommended by Einhorn and Hamburger (*loc. cit.*) for the preparation of this substance is unnecessary; by exposing for a day or two in an exhausted desiccator a solution of carbamide (1 mol.) in formalin (1 mol.), just neutralised by dilute alkali hydroxide, a viscid, crystalline paste was obtained, from which, after a couple of recrystallisations from alcohol, methylolcarbamide was isolated in brilliant, flattened prisms melting at about 110° (corr.). (Found: N = 30·9; $C_2H_6O_2N_2$ requires N = 31·11 per cent.).

The aqueous solution was odourless, and gave with sodium nitroprusside and phenylhydrazine no reaction for formaldehyde, and with neutral mercuric nitrate no reaction for carbamide. On acidification, however, formaldehyde was detected, both prior to condensation and long after the process appeared to be complete.

Dimethylolcarbamide.

A neutralised solution of carbamide (1 mol.) in a little more than 2 mols. of formalin, when treated as above, yielded dimethylolcarbamide; it had essentially the properties described by Einhorn and Hamburger, including the relatively slow condensation by acids. In moderately concentrated solutions, this process requires approximately minutes, where seconds are needed in the case of the monomethylol analogue. Otherwise, its behaviour in an aqueous solution was the same as that of methylolcarbamide.

The fused material soon began to decompose (m. p. about 123°), water and formaldehyde escaping, and a white, amorphous solid being left; this, when heated alongside a pure specimen of the compound, $C_5H_{10}O_3N_4$, melted at the same moment as the latter, and with similar effervescence and browning (255°, uncorr.; both introduced into the bath at 235°). By condensing an aqueous solution with dilute hydrochloric acid, the same product was obtained as by heating; it gave N = 32·8 per cent., whereas $C_5H_{10}O_3N_4$ requires N = 32·18 per cent. The end result of these changes may thus be represented:

$$2CO(NH\cdot CH_2\cdot OH)_2 \longrightarrow H_2O + CH_2O + C_5H_{10}O_3N_4.$$

Expt. 13.—Approximately pure methylolcarbamide, when condensed by means of dilute hydrochloric acid, yielded a product containing only 35·5 per cent. of nitrogen ("methylenecarbamide" requires N = 38·89 per cent.), the deficit presumably being due, as earlier suggested, to the attack of the methylolcarbamide, when in the act of yielding its normal condensation product, by the formaldehyde which is liberated before that act is complete.

The experiment was repeated, 1 molecular proportion of formaldehyde being first added to the solution of methylolcarbamide; in these circumstances, the solid product was found to consist solely of Goldschmidt's compound. (Found, N = 32·25. $C_5H_{10}O_3N_4$ requires N = 32·18 per cent.)

Expt. 14.—In order to learn whether the last-named compound might result through an interaction between the two methylolcarbamides, somewhat as follows:

$$NH_2\cdot CO\cdot NH\cdot CH_2\cdot OH + CO(NH\cdot CH_2\cdot OH)_2 \longrightarrow 2H_2O + C_5H_{10}O_3N_4,$$

a molecular mixture of the components, in aqueous solution, was acidified, the mixture (which began to condense in forty seconds) being allowed to remain overnight. Here, if the two jointly condensed, the sole product must be the material containing N = 32·18 per cent., whereas, if they condensed independently, the first precipitate would be the mixture referred to in Expt. 13 as containing N = 35·5 per cent., to which later the condensate of dimethylolcarbamide (N = 32·18 per cent.) would add itself; so that, ultimately, the product must give a figure somewhere between the two. The percentage actually found was 33·35, and when the experiment was repeated, but with 0·75 mol. of dimethylolcarbamide, the figure was 34·6; hence, it is concluded that, in a mixture of methylol- and dimethylol-carbamide, acidified with hydrochloric acid, the two substances condense independently.

Although in the acid condensation of the former, the elimination of formaldehyde prevents the production of pure "methylenecarbamide," yet fused methylolcarbamide soon decomposes, water being evolved, but little or no formaldehyde. In this case, the residue is doubtless free from much contamination with Goldschmidt's compound; no analysis, however, was made.

Expt. 15.—Solutions were prepared (*a*) of methylolcarbamide, (*b*) and (*c*) of carbamide and formaldehyde in molecular proportion. All had the same "carbamide-concentration" (1 gram in 6 c.c.); equal volumes of each, at 13°, were acidified with one-twelfth the volume of concentrated hydrochloric acid. Prior to acidification, however, (*b*) was kept at 13° for an hour and a half. The times elapsing before precipitation were, for (*a*) less than three seconds, for (*b*) twenty-eight seconds, for (*c*) forty-five seconds. Ready-made methylolcarbamide, therefore, condensed at least fifteen times as rapidly as a mixture of its components, which had remained for some five or six minutes, whilst a like mixture, kept beforehand for an hour and a-half, condensed in nearly half the time.

Evidently, the union of formaldehyde with carbamide takes place only by degrees; in fact, a solution, kept for twenty-four hours in a vacuum desiccator, still had a strong odour of formaldehyde. In the presence of barium hydroxide, too, at the concentration recommended by Einhorn and Hamburger, the same phenomenon was noticed.

CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE,
CORK.

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XXIX.—*The Sub-bromide and Sub-chloride of Lead.*

By Henry George Denham.

In a recent paper (T., 1917, **111**, 29), the author has described a method for the preparation of lead sub-iodide by the action of methyl iodide vapour on lead sub-oxide. As indicated in that paper, the method appears of a somewhat general nature, applicable at least to the preparation of other sub-salts of lead. In the present paper, the method has been used to prepare lead sub-bromide and sub-chloride, the only radical alteration being in the replacement of the methyl haloid by the ethyl compound, owing to the more convenient boiling point of the higher homologue.

Lead Sub-bromide.

The apparatus already described in the previous paper (*loc. cit.*) has, with a few minor alterations, proved quite suitable. The lead sub-oxide was prepared from lead oxalate (Found: Pb = 70·17. Calc.: Pb = 70·18 per cent.) precipitated from an acid solution of lead acetate by the addition of oxalic acid, the actual decomposition of the oxalate into the sub-oxide being carried out precisely as described in the former paper. The alterations in the apparatus to be noted were the replacement of phosphoric oxide as a drying agent by anhydrous calcium chloride, and the introduction of a contriction in the glass tubing leading from the oven to the condenser. The former was a matter of necessity, owing to a temporary shortage of the phosphoric oxide, the latter was devised to facilitate the control of the distillation. Shortly after the ethyl bromide* had been introduced into the apparatus, a little distillate collected at the constriction and formed a most convenient gauge for noting the velocity of distillation. This is a very

* *Purification of the Ethyl Bromide.*—The ethyl bromide was prepared from chemically pure potassium bromide, ethyl alcohol, and sulphuric acid. The distillate was treated with dilute sodium carbonate solution, several times with water, then shaken at least four or five times with concentrated sulphuric acid, and finally with water (owing to a tendency to emulsify, it was often found necessary to wash several times with dilute sodium hydroxide solution before the final washing with water). The bromide was dried over calcium chloride, and fractionated from phosphoric oxide, the fraction of constant boiling point alone being used. This method of purification had to be rigidly followed, otherwise samples of ethyl bromide were obtained that contained traces of some reactive impurity in sufficient quantity to cause appreciable errors when a relatively large amount of the bromide was distilled through the sub-oxide.

essential point, for the ethyl bromide appears to react much less vigorously with lead sub-oxide than does methyl iodide. Thus, in the preparation of lead sub-iodide, about fifty minutes' distillation sufficed to convert the sub-oxide into the sub-haloid, whilst in the present case at least 150 minutes' distillation was required to secure complete reaction. The need for a preliminary heating of the vapour before it enters the reaction bulb is even more necessary than in the case of lead sub-iodide. This was again obtained by passing the vapour through a capillary spiral. The extreme slowness of the reaction naturally leads one to search closely for the temperature at which the ethyl bromide just escaped decomposition. By the process of "bracketing," it was found that the distillation can be safely carried through at 261°, but not higher. At temperatures much lower than this, the last traces of sub-oxide react very sluggishly; for example, at 258°; analysis indicated the presence of 74·1 per cent. of lead (PbBr requires Pb=72·16 per cent.), although, by the prolonged absence of the evolution of gas, the reaction appeared quite complete. At 262° gas was evolved until the end of the experiment, the product was much lighter than that obtained in experiments carried out at 261°, and analysis gave Pb=70·2 per cent. Undoubtedly there had been incipient decomposition of the bromide vapour, with liberation of bromine and subsequent oxidation of the lead sub-bromide to the normal bromide. Indeed, it may be safely asserted that whenever this evolution of gas continues throughout the experiment, one invariably obtains a product contaminated by more or less lead bromide. After the distillation was completed, the receiver containing the distillate was cooled with liquid ammonia, the apparatus partly exhausted, the receiver sealed off, and the exhaustion continued until the pressure had fallen to about 1 mm. It was found to be unnecessary to continue the exhaustion longer as several experiments showed no trace of a volatile product, such as occurred in the preparation of lead subiodide. On the other hand, the amount of non-volatile carbonaceous matter was sufficiently high to necessitate estimation, generally amounting to from 0·3 to 0·5 per cent. of the weight of the lead sub-bromide.

Method of Analysis.—The mixture of lead sub-bromide, carbonaceous matter, and silica was digested with concentrated acetic acid, then extracted with water; after four extractions the residue was treated with a little hot, very dilute nitric acid, as it was found that the carbonaceous matter otherwise tended to coagulate and retain traces of lead bromide. Two washings with the dilute nitric acid sufficed to remove the whole of the dissolved bromide. The

bromine was then weighed as silver bromide; the silica and carbon were weighed in a Gooch crucible, and after ignition in a muffle the weight of carbon was obtained by difference.

The analytical details of the accompanying experiment will make clear the use to which the knowledge of the percentage of carbon was put in arriving at the percentage of lead in the sample.

Typical Experiment.

Two bulbs each containing about 5 grams of lead oxalate intimately mixed with 2 to 3 grams of powdered silica.

Decomposition took place at a maximum temperature of 340° and maximum pressure of 5 cm. Ethyl bromide: about 15 c.c. Temperature of distillation, 261°. *Remarks.*—Five c.c. of distillate had collected in sixty-five minutes. No gas evolution for the last forty minutes. Duration of distillation, one hundred and thirty-five minutes.

Estimation of Lead:—

Weight of bulb and contents	= 8·6648
„ „ „	= 3·7758
„ „ carbon, silica, bromide	= 4·8890
Corrected for air displacement	= 4·8910
Weight of silica	= 4·4039
„ „ carbon (calculated from Br analysis)	= 0·0017
„ „ bromide used	= 0·4854
„ „ lead sulphate	= 0·5148
Percentage of Pb	= 72·46

Estimation of Bromine:—

Weight of bulb and contents	= 8·6020
„ „ „	= 3·4394
„ „ carbon, silica, bromide	= 5·1626
Corrected for air displacement	= 5·1644
„ carbon and silica	= 4·4927
„ substance	= 0·6717
„ AgBr found	= 0·4424
Percentage of Br	= 28·3

Synopsis of Results.

Experiment.	Duration of distillation.	Absence of gas evolution for	Pb. Per cent.	Br. Per cent.
1	135 min.	40 min.	72·5	28·0
2	122 „	20 „	71·7	28·4
3	140 „	25 „	71·6	27·5
4	180 „	60 „	72·5	27·3
5	180 „	20 „	72·5	28·4
6	175 „	20 „	71·7	28·2
7	135 „	50 „	71·8	28·0
8	135 „	65 „	72·6	28·0
9	155 „	90 „	71·9	27·9
		Mean	72·09	27·97
		Calc.	72·16	27·84

The slight fluctuations about the mean undoubtedly arise from the extreme difficulty in (*a*) securing complete absence of oxygen, not only in preparing the sub-oxide, but in the introduction of the ethyl bromide and in the distillation, for example, 0·1 c.c. of oxygen let into the apparatus would cause an error of nearly 0·2 per cent. in the estimation of bromine; (*b*) maintaining the temperature of the oven just below that of incipient decomposition during distillation; and (*c*) securing sufficiently slow velocity of distillation to secure thorough heating of the vapour throughout a lengthy experiment.

Properties of Lead Sub-bromide.—The substance oxidises very slowly, more rapidly if the air is moist. After boiling with water in the air and filtering, very little evidence is obtained in the filtrate either of lead or of bromine, whilst if a saturated solution of the sub-bromide is prepared in the absence of air, there is obtained with hydrogen sulphide a darkening in the colour of the solution, but no precipitate separates; under similar conditions lead bromide gives a heavy, black precipitate. A saturated solution prepared in a vacuum gives with silver nitrate only a faint opalescence.

The colour of the sub-bromide appears to be a distinct gray, and although the presence of 0·3 to 0·5 per cent. of carbonaceous matter must necessarily darken the colour, there is little doubt that the grayish appearance is characteristic of the sub-bromide for the following reasons: (*a*) Whenever analysis gives a higher percentage of bromine than 27·9, that is, whenever oxidation has occurred through the temperature being sufficiently high to liberate bromine from the ethyl bromide with consequent oxidation of the sub-bromide to the normal bromide, the colour changes to a much paler one, the substance becoming at times nearly white.

After a rapid distillation carried out at 300° the product was found to be a pale gray, although the percentage of bromine did not exceed 30·6.

Moreover, such a pale coloured product gives, on extraction with hot water, a copious precipitate with a solution of silver nitrate, a reaction which totally fails when the gray product is used.

(*b*) On heating gray lead sub-bromide in a vacuum for two hours at 370°, the colour becomes distinctly paler, and a rapid extraction with hot water reveals the presence of a considerable amount of lead bromide.

The sub-bromide slowly decolorises bromine water, rapidly on warming to about 50°. The sub-bromide, on treatment with acetic acid, nitric acid, etc., immediately decomposes into lead and lead bromide, and after diluting and boiling, complete solution takes place, except for a small quantity of carbonaceous matter.

Determination of Solubility.—As a further proof of the individuality of the compound, the determination of the solubility of the salt in a vacuum by the conductivity method was used. The apparatus already figured (*loc. cit.*) was again used. Small bulbs of thin glass containing silica and about 0·1 gram of lead sub-bromide were prepared by the usual method, and the purity of the samples was controlled by the analysis of the contents of larger bulbs. The actual procedure already described (*loc. cit.*) was closely followed.

The resistance of a saturated solution of carefully prepared lead bromide at 25° was found to be 22 ohms, remaining constant for two hours.

The mean of two closely agreeing experiments with lead sub-bromide gave the following results:

Resistance of the water before breaking the bulb.....	=	26000 ohms.
After breaking the bulb.....	=	1860 „

this remaining unchanged for several hours.

If the ionic mobilities of the bromine and the lead ions (whether Pb^{+} or Pb_2^{++}) are assumed to be the same as in the case of the normal bromide (76·6 and 71·8 respectively), and if complete dissociation takes place, the solubility of the sub-bromide is 0·4 milli-equivalent per litre. This value is about the same as that for the subiodide already recorded (0·35 milli-equivalent per litre), but in both cases it must be emphasised that the values obtained for the solubility are probably a little high, due to unavoidable traces of the normal salt. Such traces are almost certain to be formed through the action of heat on the sub-salt during the sealing of the bulb, whilst the carbonaceous matter, too, may exert an influence on the solubility.

Lead Sub-chloride.

When the lead oxalate has been completely decomposed into sub-oxide about 10 grams of ethyl chloride thoroughly cooled by liquid ammonia were introduced into the distillation flask. By this means any desired quantity could be rapidly introduced from the tubes. The distillation of the chloride could be rapidly regulated by adjusting the temperature of the water-bath, but owing to the low boiling point of the chloride no effort was made to collect the distillate. The reaction between the sub-oxide and the vapour of the ethyl chloride was very slow, and it was soon found that approximately three hours were required for the distillation and a temperature as high as 311° (as recorded by a standardised thermometer). This is shown in the following table.

TABLE I.

Experiment.	Temperature.	Duration.	Cl. Per cent.
1	261°	85 min.	4·2
2	275	135 „	7·4
3	300	165 „	11·1
4	310–11	165 „	14·4
5	312	160 „	15·0
6	315	180 „	17·2
		Theoretical ...	14·6

The highest temperature at which the distillation may be carried out appears to be 311°, and the duration of the experiment in the neighbourhood of three hours. The slowness of reaction suggested that it might be possible to carry through the experiment without having silica present, as was the case with the sub-iodide. In two experiments it was impossible to detect any difference between samples prepared in the presence and in the absence of silica, and in the majority of the experiments tabulated in table II silica was not used as diluent. The only other change in the procedure was that phosphoric oxide was again used as a drying agent, in order to eliminate any traces of ammonia absorbed by the ethyl chloride when it was being introduced into the apparatus.

Method of Analysis.—A slight modification in the method of estimating lead was necessary owing to the high percentage of carbonaceous matter retained in the reaction bulbs. As a rule the estimation of chlorine revealed the presence of about 2 per cent. by weight of carbonaceous matter. The low value at first found by the old method in the estimation of lead under conditions when the estimation of chlorine led one to expect that a pure

sample of sub-chloride had been obtained, suggested that this carbonaceous matter, impregnated as it would be with lead sulphate, might be exercising a reducing action with a consequent slight loss of lead. Thus in one experiment the percentage of chlorine found was exactly correct, whilst the percentage of lead was 84·4 (calc., 85·4). Two bulbs were then prepared, the lead in one being estimated by the method already described; in the other the sub-chloride was extracted five times with hot dilute nitric acid, the filtrate concentrated in a weighed silica crucible, and finally evaporated with excess of sulphuric acid. The results by the old and the new methods were respectively 83·6 and 85·1 per cent., a duplicate experiment giving identical results. The results recorded in table II were obtained by the modified method for estimating lead, the percentage of chlorine being obtained in a manner similar to that described for the bromide, except that no estimation of silica was necessary.

The analytical results are given in table II.

TABLE II.

Experiment.	Duration of distillation.	Pb. Per cent.	Cl. Per cent.
10	190 min.	85·14	14·24
11	205 „	85·30	14·85
12	165 „	85·53	14·90
13	210 „	85·11	14·60
14	210 „	85·17	14·04
15	180 „	85·94	14·91
	Mean	85·36	14·59
	Theoretical ...	85·39	14·61

Properties of Lead Sub-chloride.—The colour of the sub-chloride is closely similar to the gray colour of the sub-bromide. It must again be emphasised that the gray appearance does not arise from the presence of the carbonaceous matter, for if the sub-chloride is heated in a vacuum above 400°, it becomes nearly white owing to the reaction:

$$2PbCl \longrightarrow PbCl_2 + Pb,$$

the whiteness of the normal chloride more than compensating for the darkness arising from the presence of an equivalent quantity of lead. The sub-chloride is fairly stable in air, but rapidly decolorises bromine water and permanganate solution.

A saturated aqueous solution of lead sub-chloride prepared in a vacuum gives a faint precipitate with silver nitrate as well as with hydrogen sulphide, strongly contrasting in this respect with

the less readily soluble sub-bromide and sub-iodide. The sub-salt is also readily decomposed by acids.

Determination of Solubility.—As a quantitative proof that the gray substance is not an intimate mixture of lead and lead chloride in molecular quantities, a comparison of its solubility with that of the normal chloride has been made by the conductivity method already described.

Resistance of a solution of lead chloride, three times recrystallised, at 25° = 15·9 ohms, a second determination giving the same result.

A small bulb containing 0·1 gram of lead sub-chloride was broken in a vacuum.

Resistance before the bulb was broken	=	21000 ohms.
„ after „ „ „ „	=	340 „

If one assumes the ionic mobilities of the lead and chlorine ions to be the same as for the normal chloride (71·8 and 75·5 respectively) and that complete dissociation takes place (highly probable if the constitution of the salt is represented by the formula PbCl, but subject to correction if the formula should prove to be Pb_2Cl_2), the solubility is found to be 2·2 milli-equivalents per litre.

Summary.

1. Lead sub-chloride and lead sub-bromide have been prepared by the action of ethyl chloride or bromide vapour at 311° and 261° respectively on lead sub-oxide.

2. Both compounds are grey, sparingly soluble, fairly stable in air, but readily oxidised by bromine water.

3. The sub-chloride has a solubility of about 2·2 milli-equivalents per litre, the sub-bromide 0·4 milli-equivalent per litre.

4. The sub-salts are readily decomposed by acid into the normal salt and metal.

Further work on the sub-salts of lead, etc., is still in progress. The author desires to record his appreciation of the facilities placed at his disposal by the Walter and Eliza Hall Trust for the prosecution of this research.

CHEMICAL LABORATORY,
UNIVERSITY OF QUEENSLAND,
BRISBANE.

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XXX.—*The Structure of Crystalline β-Methylfructoside.*

By Ettie Stewart Steele.

Considering the part played by fructose as a constituent of natural disaccharides and polysaccharides, the simple condensation reactions of the sugar are invested with a special importance. The prosecution of these studies is, however, seriously handicapped by the fact that few crystalline compounds are known to result from such condensations, and further complication is introduced by the recent observation that fructose may react in two forms, one of which is constituted according to the ethylene–oxide type of sugar (Irvine and Robertson, T., 1916, **109**, 1305).

Taking these factors into account, it is evident that the examination of the formation of fructosides is beset with difficulties. Thus, the action of acid methyl alcohol on fructose leads to the production of an uncrystallisable syrup, which Fischer (*Ber.*, 1895, **28**, 1145) originally regarded as essentially methylfructoside, and that this product was a mixture of isomeric fructosides was afterwards shown by Purdie and Paul (T., 1907, **91**, 289), who traced the progress of the condensation by polarimetric observations. The complexity of the reaction between fructose and methyl alcohol was further indicated by the fact that, on methylation followed by hydrolysis, the above mixture of fructosides gave rise to two distinct forms of tetramethyl fructose, one of which is crystalline and the other a colourless syrup. The optical relationships of the solid variety of tetramethyl fructose corresponded with those which might reasonably be expected on the assumption that, during the formation of methylfructoside, the parent sugar had reacted partly in the normal butylene–oxide form, and that this structure was preserved in the alkylated ketose. On the other hand, the nature of the syrupy isomeride remained obscure until it was recognised that fructose, in common with other reducing sugars, is capable of reacting in an entirely different form, containing presumably the ethylene–oxide linking. These views have already received expression (Irvine and Robertson, *loc. cit.*), and the explanation has been put forward that the syrupy methylfructoside described by Fischer contains four isomeric compounds, two of which are derived from the normal and two from the abnormal forms of the parent sugar.

The isolation by Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1216) of a definite crystalline variety of methylfructoside presents an opportunity to test these views and thus to correlate the results of

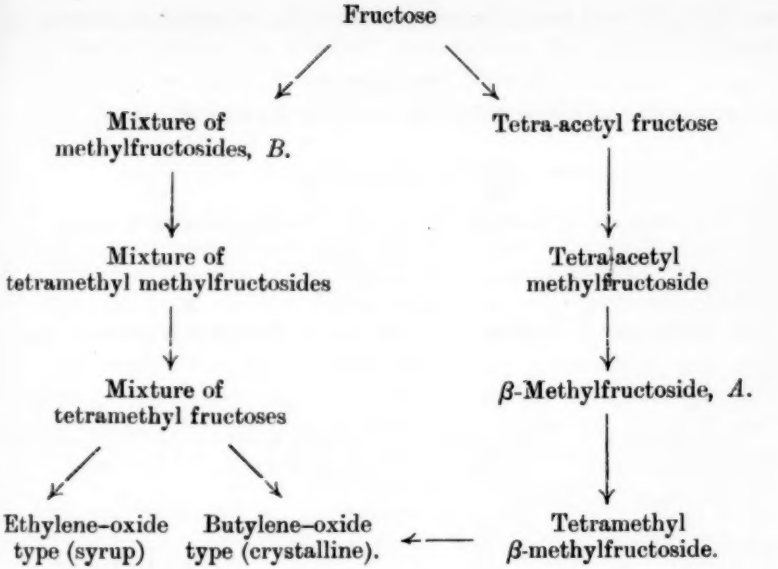
the different workers in this field. By ascertaining the behaviour of this pure solid fructoside towards potassium permanganate solution, it has now been shown that the compound belongs to the stable type, and thus corresponds with the ordinary α- or β-varieties of methylglucoside, and the magnitude of the specific rotation of the compound is in agreement with this view. With this point settled, it has been possible to prove that the crystalline variety of tetramethyl fructose is likewise a derivative of the butylene–oxide form of fructose. The proof consists in the fact that Hudson's methylfructoside, on complete methylation and hydrolysis, is converted into a crystalline tetramethyl fructose identical with one of the products obtained by Purdie and Paul on subjecting syrupy methylfructoside to the same series of reactions.

It is thus possible to complete the interpretation of the somewhat complex reactions involved in the condensation of fructose with methyl alcohol. The sugar reacts in large measure in the ethylene–oxide form, giving rise to a highly reactive methylfructoside, but, at the same time, normal condensation takes place to a more limited extent. The condensation must thus resemble in many ways that involved in the formation of sucrose, as it has been shown that the fructose constituent of the disaccharide conforms to the ethylene–oxide sugar type (Haworth and Law, T., 1916, **109**, 1314). There is, in fact, an accumulation of evidence pointing to the idea that most fructose derivatives are constituted according to this plan, but, as already stated, a notable exception is provided by Hudson's crystalline methylfructoside and the tetra-acetyl fructose from which it is prepared, as these compounds are undoubtedly representatives of the stable butylene–oxide type.

The complete relationship between the reactions now correlated may be expressed in the scheme on page 259.

The definite compound *A* is thus a constituent of the mixture *B*, and is the source of crystalline tetramethyl fructose of the stable type.

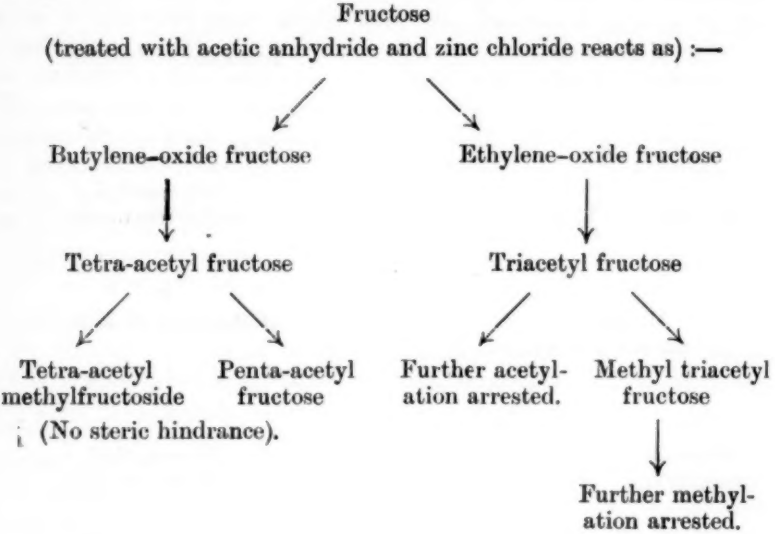
Incidentally, in the course of the work a certain amount of fresh information has been gained as to the action of acetic anhydride and zinc chloride on fructose. Hudson's view that the reaction yields the tetra-acetate as an intermediate step in the formation of the penta-acetate has been supported. The yield of tetra-acetyl fructose is, however, only moderate even under the best conditions, and a considerable quantity of an uncrystallisable syrup is formed which has the composition of a triacetate. This was at first regarded as a mixture of partly acetylated fructoses, but as the composition and specific rotation were not altered by further action with acetic anhydride or by fractional treatment with solvents, it



would appear to be a definite chemical individual. The compound showed the instantaneous reaction towards potassium permanganate solution which is characteristic of the ethylene–oxide type of sugars, and considering the special reactivity of such compounds, the resistance towards complete acetylation is remarkable. This steric hindrance also extends in some measure to alkylation, as, by treatment with silver oxide and methyl iodide, only one methyl group could be introduced into the compound, although two hydroxyl groups are presumably available for substitution.

In sharp contrast with these results, the crystalline tetra-acetyl fructose of the butylene–oxide type displays no resistance to complete substitution, as it can be readily converted into one variety of penta-acetyl fructose and also forms a fully acetylated methyl fructoside. In one respect, however, the compound is abnormal in that, although belonging to the butylene–oxide type and a true reducing sugar, it fails to display mutarotation. This has already been noted by Hudson, and is now confirmed in so far as repeated attempts to isolate the compound in mutarotatory forms invariably failed. In one sense, it is disappointing to find that tetra-acetyl fructose does not belong to the ethylene–oxide type, as the possibility seemed open that the compound might provide a suitable reagent for the synthesis of sucrose. The structural relationships of the compound, as now elucidated, are shown below, and, taken in conjunction with the constitutional study of sucrose contributed

by Haworth and Law (*loc. cit.*), render this expectation somewhat remote.



Experimental.

Preparation and Methylation of β-Methylfructoside.

The fructose employed was specially pure crystalline material prepared for bacteriological use by the hydrolysis of inulin. The sugar was converted into tetra-acetyl fructose in the usual way and thereafter methylated so as to produce tetra-acetyl β-methylfructoside. On removal of the acetyl groups by the agency of barium hydroxide, pure β-methylfructoside was obtained as described by Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1216).

To a methyl-alcoholic solution of the fructoside (1 mol.) were added silver oxide (5 mols.) and methyl iodide (10 mols.) in the usual way, and the alkylation, which proceeded normally, was completed by six hours' warming on a water-bath. After filtration from silver iodide and extraction of the residue with boiling methyl alcohol, the solution was evaporated under diminished pressure to a syrup and the total product subjected to a second alkylation, in which the same proportion of the methylating agents was used. In this case no extraneous solvent was necessary as the syrup was freely soluble in methyl iodide. On isolation of the product, tetramethyl β-methylfructoside was obtained as a colourless, mobile syrup, showing practically no action on Fehling's solution until after hydrolysis. The compound was identical with that obtained

by Purdie and Paul by condensing crystalline tetramethyl fructose with methyl alcohol by Fischer's method and the specific rotation displayed by the two preparations show little divergence.

Solvent: methyl alcohol; $c=1{\cdot}220$; $[\alpha]_D -120{\cdot}1$.

Hydrolysis of Tetramethyl β-Methylfructoside.

A 3 per cent. solution of the methylated fructoside in 1·5 per cent. aqueous hydrochloric acid was hydrolysed by heating at 90° for thirty minutes. The solution was neutralised by means of barium carbonate, filtered, evaporated to dryness under diminished pressure, and the residue extracted with boiling ether. After drying and removal of the solvent, the syrup obtained in this way solidified completely to a mass of square plates. After two crystallisations from light petroleum the sugar melted at 92—95°, and showed downward mutarotation in the lævo sense, the permanent value being $[\alpha]_D -85{\cdot}6$. The corresponding constants quoted by Purdie and Paul are m. p. 98—99° and $[\alpha]_D -86{\cdot}7$. It is to be observed, however, that this maximum melting point refers to the pure stereoisomeride, and is thus attained only after repeated crystallisation. An average specimen of tetramethyl fructose melts in the neighbourhood of 95°, and the specimen now described showed no alteration in melting point when mixed with material prepared by Purdie and Paul. The composition of the sugar was confirmed by analysis. (Found, OMe=50·65. $C_6H_8O_2(OMe)_4$ requires OMe=52·54 per cent.)

Action of Acetic Anhydride and Zinc Chloride on Fructose.

Fifty grams (1 mol.) of pure crystalline fructose were added gradually to a solution of 4·5 grams of zinc chloride in 250 c.c. (10 mols.) of acetic anhydride and the mixture was stirred at 0° until the fructose had dissolved. The acetylated sugar was extracted with chloroform as described by Hudson, whereby 45 grams of crystalline material were obtained. Recrystallisation from 98 per cent. alcohol yielded 31·8 grams of pure tetra-acetyl fructose. This compound melted at 129—130°, showed $[\alpha]_D$ in chloroform $-92{\cdot}30$, and did not affect potassium permanganate solution even on prolonged action. Attempts to detect mutarotation in chloroform or aqueous solutions of the compound gave negative results even when chloroform or water were substituted for alcohol as the recrystallising media. The tetra-acetyl fructose obtained in this way showed a constant specific rotation in all appropriate solvents.

Examination of Triacetyl Fructose.—After removal of all crystal-

lisable tetra-acetyl fructose from the product of the preparation just described, a large proportion (47 grams) of syrup remained. In order to remove acetic anhydride, this material was boiled for twelve hours under reflux with a large excess of pure dry methyl alcohol. The solution was then neutralised with barium carbonate, and, after filtration, concentrated in a vacuum. Extraction with chloroform gave a pale yellow syrup, having $[\alpha]_D$ in chloroform $-20{\cdot}42$. Analysis of the syrup, dried in a vacuum, gave an acetyl content of 40·41 per cent., which agrees approximately with the calculated value for a fructose triacetate (42·15 per cent.). Attempts to effect further acetylation of the triacetate by repeating the action of acetic anhydride and zinc chloride in the cold failed entirely. The same proportion of the acetylating reagent was used as in the preparation of tetra-acetyl fructose, and the mixture was stirred at 0° until a homogeneous system was obtained. Examination of the product showed it to be unaltered in composition or specific rotation. Further evidence that the syrup was a homogeneous compound was afforded by the fact that fractional extraction with solvents failed to separate the material into components showing any differences in rotatory power.

The exact constitution of the compound has not been determined, and it is even impossible to characterise it with certainty as a genuine derivative of fructose. The removal of the acetyl groups required prolonged agitation in the cold with $N/10$-barium hydroxide, the unsubstituted sugar thus obtained being a lævorotatory syrup. This, although readily convertible into phenylglucosazone melting at 203—204°, could not be identified as fructose, and, considering the conditions required for the hydrolysis of the triacetate, was doubtless an equilibrium mixture of glucose, fructose, and mannose.

Methylation of Triacetyl Fructose.

The syrup dissolved readily in methyl iodide and was methylated in the usual manner with the following proportions of the reagents: triacetyl fructose (1 mol.), silver oxide (5 mols.), and methyl iodide (10 mols.). After a second alkylation the product, isolated in the usual manner, was a colourless syrup, which reduced Fehling's solution and was therefore not a derivative of methylfructoside. As the most trustworthy indication of composition is given by the methoxyl and acetyl contents, these values were determined. Found, OMe = 10·6; OAc = 42·86.

$C_6H_8O_2(OMe)(OAc)_3$ requires OMe = 9·7; OAc = 42·15 per cent.

Solvent.	c.	Specific rotation.
Chloroform	2·504	−21·96
Ethyl alcohol	2·230	−21·07

The methylated derivative has thus the composition of a monomethyl triacetyl fructose.

The author desires to express her indebtedness to the Carnegie Trust for a research scholarship, during the tenure of which the above research was conducted, and also to Dr. C. S. Hudson, of the U.S. Department of Agriculture, for specimens of various fructose derivatives which facilitated the work.

CHEMICAL RESEARCH LABORATORY,
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

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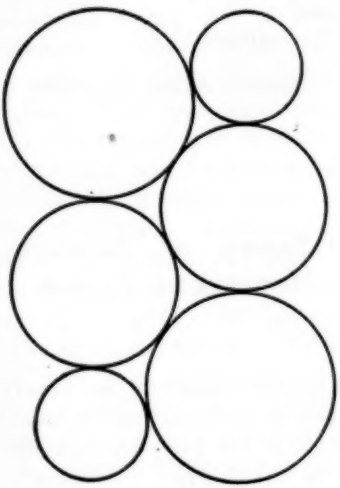
XXXI.—*Contributions to the Theory of Solutions. Solubility Studies in Ternary Mixtures of Liquids.*

By JOHN HOLMES.

AN explanation of the property of relative solubility in binary mixtures of liquids has been put forward in previous papers, based on the ascertained difference in magnitude of the molecular volumes of the constituents of the mixture. It was deduced mathematically that so long as the ratio of the radii of the respective molecules—assuming them to be capable of representation by a spherical surface—did not exceed the proportion 1·618 : 1, the liquids would be miscible in all proportions, and, when the ratio became greater than this value, the mixture would separate into two layers, in each of which the selective distribution of molecules depends on the further increase of this factor until it reaches 2·414 : 1, when the liquids are now completely immiscible. In practice, the relative solubilities of commonly known liquids were found to be in close agreement with these theoretical deductions, and it seemed reasonable to expect that the extension and application of the same principle to three-component systems would afford an explanation of the somewhat similar solubility phenomena therein observed.

Provided that no chemical interaction occurs between the constituents of a ternary mixture of liquids and that no individual liquid influences by its simple physical presence the other constituents, any three liquids the molecular spheres of which have equal radii should be miscible in all proportions. When the spheres are of different sizes, as the ratios of the several radii

increase, the dimensions of the interspaces decrease in magnitude until, as in the case of binary mixtures, a point is reached at which close packing is a maximum. In an equimolecular mixture, which lends itself more readily to mathematical demonstration, this occurs when the radii are as 1·682 : 1·466 : 1 (see Figure). It is suggested that when these conditions are fulfilled, the liquids are on the border line between complete and partial miscibility, and that, so long as the ratios between the several radii are not greater than these values, the liquids will be mutually miscible in all proportions. When, however, the respective ratios are greater in magnitude, a complex is formed which will not allow of the same close-packing, but results in the formation of layers of liquid the relative proportions of which depend on the difference in these ratios.



Relative radii, 1 : 1·466 : 1·682.

A further consequence of this method of reasoning follows from the known ratio of radii required for the critical point of solution in binary mixtures. So long as the value of the radial ratio of the two smaller molecules is not greater than 1·618, and the corresponding radius of the larger molecule is greater than 1·682 and does not exceed $(1{\cdot}618)^2$, the mixture should separate into two layers only, but if, on the other hand, the respective ratios are greater than these values, and the greater ratio exceeds the less by more than 1·618 times its value, then the liquids should fall out into three distinct and stable layers.

The object of this communication is to present the results of a preliminary examination into the behaviour of ternary mixtures of liquids from the point of view of these theoretical considerations and of the hypothesis on which this simple law of mixtures is based.

Experimental.

In order to determine the critical point of solution in three-component systems, binary mixtures of liquids were first prepared in equimolecular proportions, and the third liquid then added in

quantity sufficient to produce a permanent cloudiness after vigorous shaking. The point of complete miscibility is capable of determination with a high degree of accuracy, since an excess of one drop in a total volume of 25 c.c. invariably causes separation into layers. The several mixtures were made in calibrated stoppered burettes suspended in a water-bath, the temperature of which was kept constant at 15°. Most of the liquids experimented with had been obtained from Kahlbaum, and the usual methods were resorted to for determining their purity.

Mixtures of the lower primary alcohols with water were prepared in equimolecular proportions referred to the gaseous state. The densities of these mixtures at 15·5°/15·5° were found to be CH_4O aq. (1/1) 0·8898, C_2H_6O aq. (1/1) 0·8676, and C_3H_8O aq. (1/1) 0·8601. The radii of the molecular spheres of methyl alcohol, ethyl alcohol, and *n*-propyl alcohol—represented by the cube roots of the quotients of molecular weight by density—are 1·3, 1·5, and 1·6 respectively when compared with that of water at 15°.

As was to be expected, formic acid, acetic acid, acetone, pyridine, and liquids generally which are miscible in all proportions with water, are similarly miscible with each of the above aqueous-alcoholic mixtures. This applies also to *iso*butyl alcohol, ethyl acetate, aniline, ethyl ether, and the amyl alcohols, the several radii of which are in slight excess of the theoretical value (1·68).

The following are some of the more important quantitative results obtained.

Mixtures with Aniline.

Proportion by volume of the constituents of the mixture.	Critical molecular mixture.
10 c.c. CH_4O aq. (1/1), 16·1 c.c. C_6H_7N, 3·2 c.c. H_2O	$C_6H_7N : CH_4O : 2·0\ H_2O$
10 c.c. C_2H_6O aq. (1/1), 12·3 c.c. C_6H_7N, 5·2 c.c. H_2O	$C_6H_7N : C_2H_6O : 3·1\ H_2O$
10 c.c. C_3H_8O aq. (1/1), 10·0 c.c. C_6H_7N, 5·7 c.c. H_2O	$C_6H_7N : C_3H_8O : 3·9\ H_2O$

The effect of the addition of small quantities of water to these critical mixtures, on the relative proportions of the layers of liquid formed, is very marked. For instance, 20 c.c. of the critical mixture with CH_4O aq. (1/1), to which were added 1·8 c.c. of water, gave after vigorous shaking an upper layer of 6·5 c.c., and a lower layer, coloured with aniline, of 15·3 c.c. Similarly, 20 c.c. of the critical mixture with C_2H_6O aq. (1/1), together with an excess of

1·0 c.c. of water, gave an upper layer of 4·4 c.c., and with 1·9 c.c. of water an upper layer of 7·1 c.c., both lower layers being coloured with aniline. The addition of 2·0 c.c. of water to 20 c.c. of the critical mixture with C_3H_8O aq. (1/1) resulted in an upper layer of 15·5 c.c., which retained the aniline colour, whilst the lower layer was practically colourless; this is the reverse of what happens in the corresponding CH_4O aq. (1/1) mixture. Results very similar to these in character were obtained in other ternary mixtures.

Mixtures with n-*Amyl Alcohol.*

Proportion by volume of the constituents of the mixture.	Critical molecular mixture.
10 c.c. CH_4O aq. (1/1), 19·25 c.c. $C_5H_{12}O$, 3·55 c.c. H_2O.	$C_5H_{12}O : CH_4O : 2·1H_2O$.
10 c.c. C_2H_6O aq. (1/1), 14·65 c.c. $C_5H_{12}O$, 3·95 c.c. H_2O.	$C_5H_{12}O : C_2H_6O : 2·6H_2O$.
10 c.c. C_3H_8O aq. (1/1), 12·0 c.c. $C_5H_{12}O$, 3·7 c.c. H_2O.	$C_5H_{12}O : C_3H_8O : 2·9H_2O$.

The critical molecular mixture of the system ethyl ether with C_2H_6O aq. (1/1) was found to be $C_4H_{10}O : C_2H_6O : 2·6H_2O$, a concentration practically the same as that obtained in the corresponding *n*-amyl alcohol mixture.

Mixtures of the foregoing liquids in equimolecular proportions afford no evidence therefore of separation into layers at 15°.

The complexities of ethyl ether and *n*-amyl alcohol, as well as those of the other liquids experimented with above, have been found to be similar to that of water (T., 1913, **103**, 2147); or, if $(H_2O)_n$ be taken as representing the molecule of water in the liquid state, the value of n is the same when applied to the usual formulæ of the other liquids—$(C_5H_{12}O)_n$, $(C_6H_7N)_n$, $(CH_4O)_n$, etc. As will be noticed in the table of liquid complexities given in the communication mentioned above, ethyl ether and *n*-amyl alcohol have molecular volumes greater in magnitude than those of the other liquids in question, and correspondingly greater radii (1·8 approx.) as compared with that of water. This value is somewhat greater than the theoretical (1·68) required for complete solution. This behaviour is analogous, however, to that observed in binary mixtures of liquids in which the critical point of solution varies within somewhat similar limits, according to the nature of the constituents of the mixture and the magnitude of the volume change which occurs on mixing. That such deviation from theoretical requirements should be obtained was therefore to be expected, since most of these mixtures afford volume changes which vary in degree in different mixtures, and must inevitably result in

some disturbance in the initial relationship of the several molecular spheres.

The admixture of the same aqueous-alcoholic mixtures with liquids having molecular radii greater than 1·8, such as methyl iodide, chloroform, benzene, xylene, carbon disulphide, etc., was found to result in the formation of two layers of liquid. The quantitative data obtained in some of these mixtures are as follows:

Mixtures with Methyl Iodide.

Proportion by volume of the constituents of the mixture.	Critical molecular mixture.
20 c.c. CH_4O aq. (1/1) : 1·55 c.c. CH_3I,	$H_2O : CH_4O : 0·03\ (CH_3I)_2$.
20 c.c. C_2H_6O aq. (1/1) : 6·8 c.c. CH_3I,	$H_2O : C_2H_6O : 0·20\ (CH_3I)_2$.
20 c.c. C_3H_8O aq. (1/1) : 15·3 c.c. CH_3I,	$H_2O : C_3H_8O : 0·56\ (CH_3I)_2$.

Mixtures with Benzene.

20 c.c. CH_4O aq. (1/1) : 1·25 c.c. C_6H_6,	$H_2O : CH_4O : 0·02\ (C_6H_6)_2$.
20 c.c. C_2H_6O aq. (1/1) : 7·6 c.c. C_6H_6,	$H_2O : C_2H_6O : 0·16\ (C_6H_6)_2$.
20 c.c. C_3H_8O aq. (1/1) : 15·6 c.c. C_6H_6,	$H_2O : C_3H_8O : 0·40\ (C_6H_6)_2$.

Mixtures with Carbon Disulphide.

20 c.c. C_2H_6O aq. (1/1) : 2·0 c.c. CS_2,	$H_2O : C_2H_6O : 0·03\ (CS_2)_4$.
20 c.c. C_3H_8O aq. (1/1) : 7·9 c.c. CS_2,	$H_2O : C_3H_8O : 0·15\ (CS_2)_4$.

According to the method adopted in previous communications for determining liquid complexities, methyl iodide and benzene are doubly complexed as compared with water, and have molecular volumes at 15° of 6·90 and 9·84, with corresponding radial ratios of 1·90 and 2·14 respectively. In the same way, carbon disulphide was found to have four times the complexity of water with a molecular volume of 13·31, and a radial ratio of 2·37. The values given above for critical molecular mixtures are referred therefore to the liquid state. The relative proportions of these liquid molecules in the critical mixtures decrease in the same alcoholic mixture as their molecular volumes increase, whilst the solubility of each liquid increases with the molecular volume of the aliphatic alcohol present.

The critical mixtures of the same liquids with water and *iso*butyl alcohol (mol. vol. 5·1 and radial ratio 1·7) are as follows:

Proportion by volume of the constituents of the mixture.	Critical molecular mixture.
20 c.c. CS_2 : 7·65 c.c. $C_4H_{10}O$: 0·4 c.c. H_2O.	$(CS_2)_4 : C_4H_{10}O : 0·26\ H_2O$
20 c.c. C_6H_6 : 10·35 c.c. $C_4H_{10}O$: 0·6 c.c. H_2O.	$(C_6H_6)_2 : C_4H_{10}O : 0·29\ H_2O$.
20 c.c. CH_3I : 14·8 c.c. $C_4H_{10}O$: 1·1 c.c. H_2O	$(CH_3I)_2 : C_4H_{10}O : 0·38\ H_2O$.

When the liquids in any of these mixtures are present in equimolecular proportions, two layers only are formed, and their behaviour as regards solubility is in general agreement with theoretical requirements.

Of the critical mixtures containing less than equimolecular proportions, those with methyl iodide approximate most closely to the theoretical, just as those containing *n*-amyl alcohol were found to give a corresponding approximation when more than equimolecular proportions are present. The molecular radii of these two liquids, compared with water at 15°, are 1·90 and 1·82 respectively. Hence the radius of the greater molecule in an equimolecular ternary mixture, which is on the border-line between complete and partial miscibility, and of which water and a lower aliphatic alcohol are the other constituents, exceeds that of the smaller molecule by a value intermediate between 1·90 and 1·82, as compared with 1·68 required by theory.

Ternary Mixtures giving Three Liquid Layers.

Little information is to be found in the wide literature relating to the subject of solubility and solutions generally regarding the formation of three stable liquid layers. In commercial analysis, such mixtures are sometimes observed, as, for instance, when castor oil, petroleum, and water or dilute alcohol are shaken together, the castor oil forming an intermediate layer between the aqueous and petroleum layers, in contradistinction to the behaviour of olive oil, which dissolves in the petroleum, so that two layers of liquid only are obtained. Marsh noticed that three layers were formed in the four-component system ethyl ether–water–potassium iodide–mercuric chloride (T., 1910, **97**, 2297), and the equilibrium existing in these mixtures has more recently been investigated by Dunningham (T., 1914, **105**, 368). It is evident that such behaviour of liquids must be classed among the simple facts of solution, and will require adequate explanation by any satisfactory theory of solution. The apparent scarcity of examples of these phenomena is due probably to the fact that no explanation of them is forthcoming from the commonly accepted theories, and that there is little inducement therefore for further investigation in this direction.

According to the principles given above for a simple law of mixtures, the conditions requisite for the formation of three layers in ternary mixtures of liquids must be sought from a consideration of the relative molecular volumes of the liquids present. If the close-packing of molecular spheres in a binary mixture, in which

the ratio of radii is greater than 1·618, results in separation into two layers, it follows that the addition of a third liquid the molecular radius of which is again proportionately greater in magnitude by $(1{\cdot}618)^2$ should result in the formation of three distinct and stable layers. Stated generally, the required ratios for three-layer formation are $(1{\cdot}618+x+y)^2:(1{\cdot}618+x):1$, where x and y are positive.

The difficulty immediately arises as to where a liquid is to be found with a radius greater than that of water by at least $(1{\cdot}618)^2$ or 2·62, since this is the lowest value possible for a three-layer system of which water is one of the constituents. No liquid with so great a molecular volume is given in the table of liquid complexities referred to above. It has been found, however, that members of homologous series, which have hitherto been examined, are similarly aggregated, as, for instance, the aliphatic alcohols and acids and the alkyl iodides, and it is reasonable to assume that members of other series are similar in this respect. From a consideration of the data at present at our disposal, it should be possible to obtain a liquid of suitable molecular volume in the series of paraffin hydrocarbons. There are good grounds for believing that these liquids are doubly aggregated as compared with water (*loc. cit.*), and that their molecular radii increase from *n*-hexane (2·4), *n*-heptane (2·5), etc., as the series is ascended. In these days, the procuring of one of these higher homologues in quantity and sufficiently pure for our purpose is practically impossible. As a compromise, a sample of American petroleum was purified from unsaturated and aromatic compounds and fractionated repeatedly, so as to remove the fractions of lower boiling point. The fraction boiling between 200° and 230° was eventually taken for these experiments. The boiling points of the homologues $C_{11}H_{24}$, $C_{12}H_{26}$, and $C_{13}H_{28}$ are given as 195°, 215°, and 235°, and their calculated radii (assuming double aggregation) are 2·85, 2·92, and 2·99 respectively when compared with water at 15°. It was hoped that the fraction employed would be free from paraffins boiling below 150° (C_9H_{20}, radius 2·7), and the presence of homologues of boiling point higher than 230° is rather advantageous than otherwise to our immediate purpose. In these circumstances, the hydrocarbons present have radii much greater than that required for insolubility in water (2·414), and their relative solubilities, even in methyl alcohol and in ethyl alcohol, are so small that three well-defined and stable layers are readily obtained in the quaternary systems, potassium carbonate–water–methyl alcohol or ethyl alcohol–petroleum.

Among the liquids that have been found to be near the border-

line of complete miscibility with water are aniline, phenol, and nicotine, of which the ascertained radii are approximately 1·7, 1·7, and 1·65 respectively, and each of which is miscible in all proportions within certain limits of temperature. Mixtures of these liquids with the sample of petroleum were made in the proportions of 90, 50, and 10 per cent. by volume, and exactly one-half of the volume of water was added to each. The several liquids were measured into narrow glass tubes which could be hermetically sealed, the total volume of the mixture being from 9 to 10 c.c. in each case. By suspending these tubes in water, the behaviour of the mixtures could be observed up to a temperature of 100°.

Petroleum–Aniline–Water Mixtures.

1.	Initial proportions by volume of constituents at 15°	Petroleum	33·3
		Water	33·3
		Aniline	33·3

On vigorously shaking this mixture at 5°, three layers of liquid are obtained, the middle aqueous layer being of slightly less volume than the upper and lower layers. Between 95° and 100°, the aniline displaces the aqueous layer and rises to the middle position, which it retains after further mixing, the three layers being still practically equal in volume. Gradual cooling causes all three layers to become cloudy, proving that mutual miscibility occurs to some extent. At low temperatures, the aniline falls again to the bottom, and the original condition of equilibrium is resumed.

2.	Initial proportions by volume of constituents at 15°	Petroleum	6·7
		Water	33·3
		Aniline	60·0

The proportions of the three layers obtained after vigorous mixing at 5° are practically the same as the initial volumes. Between 95° and 100°, the aniline layer again displaces the hitherto middle aqueous layer, and on mixing at this temperature, dissolves entirely in the petroleum, thus forming two final layers of liquid. On cooling gradually, the upper petroleum–aniline layer becomes cloudy at 76°, and separates rapidly into two layers, the aniline approaching in volume to its initial proportion and taking up the middle position between the petroleum and aqueous layers. On further cooling, the aniline eventually falls to the bottom into its original position.

3.	Initial proportions by volume of constituents at 15°	Petroleum	60·0
		Water	33·3
		Aniline	6·7

At 5°, the respective layers have the relative proportions

Petroleum layer	62
Water layer	33 .
Aniline layer	5

At 95°, the aniline rises to the middle position and dissolves in the petroleum, forming two layers of liquid. On cooling, the upper layer becomes cloudy again at 55°, and the subsequent behaviour of the mixture on further cooling is similar to that of the preceding mixtures.

Petroleum–Phenol–Water Mixtures.

1. Initial proportions by volume of constituents at 45°

Petroleum	33·3
Water	33·3
Phenol	33·3

On vigorously shaking this mixture at 5°, three layers of liquid are obtained having the approximate proportions

Petroleum layer	35
Water layer.....	22
Phenol layer	43

At 90°, the water and phenol are mutually miscible and form with the petroleum a two-layer system. On cooling, the lower aqueous layer becomes cloudy at 71°, and, at immediately lower temperatures, concentrated phenol separates and falls to the bottom, forming three layers again.

2. Initial proportions by volume of constituents at 45°

Petroleum	6·7
Water	33·3
Phenol	60·0

After mixing at 5°, the relative proportions of the three layers are approximately

Petroleum layer	7
Water layer	13.
Phenol layer	80

Vigorous shaking at 90° results in the formation of two layers of liquid. On cooling, the lower aqueous-phenol layer becomes cloudy at 49°, when concentrated phenol commences to fall to the bottom, and three layers are again obtained.

3. Initial proportions by volume of constituents at 45°

Petroleum	60·0
Water	33·3
Phenol	6·7

At 5°, the relative proportions of the three layers obtained after mixing are

Petroleum layer	62
Water layer	31.
Phenol layer	7

Above 63°, two layers only are

formed, but below this temperature phenol separates, and three stable layers are again obtained.

Petroleum–Nicotine–Water Mixtures.

1. Initial proportions by volume of constituents at 15°

Petroleum	33·3
Water	33·3
Nicotine	33·3

After vigorous shaking at 5°, this mixture of liquids separates into two layers having the relative proportions

Petroleum layer	36
Aqueous-nicotine layer ...	64

When the mixture is heated to 62°, the lower aqueous layer becomes cloudy and separates rapidly into two layers, a lower layer coloured with nicotine and an intermediate and practically colourless aqueous layer which increases in volume as the temperature rises until, at 90°, the relative proportions are

Petroleum layer	41
Water layer	26
Nicotine layer	33

On mixing at the latter temperature, two layers are again formed, due to the nicotine dissolving in the petroleum. The observed proportions of the layers were now

Petroleum–nicotine layer	67
Aqueous layer	33

Both layers remain clear at temperatures above 63°, but at immediately lower temperatures the nicotine begins to separate from the petroleum and falls to the bottom of the tube, leaving at first a colourless intermediate aqueous layer, which, however, on further cooling, mixes with the nicotine, and the liquids resume their original equilibrium of two layers.

2. Initial proportions by volume of constituents at 15°

Petroleum	6·7
Water	33·3
Nicotine	60·0

At 5°, this mixture of liquids forms two layers in the relative proportions

Petroleum layer	8
Aqueous-nicotine layer	92

On raising the temperature to 67°, a cloudiness appears in the aqueous layer, and three layers are formed which at 90° have the relative proportions

Petroleum layer	8
Aqueous layer	9
Nicotine layer	83

. At 100°, the lower nicotine layer rises to

the middle position and dissolves in the petroleum, so that on mixing at this temperature two layers again are formed in the proportions

Petroleum–nicotine layer...	75
Aqueous layer	25

On cooling, the nicotine commences to separate from the petroleum and fall to the bottom of the tube at 68°, and its general behaviour at lower temperatures is similar to that in the preceding mixture. Very gradual cooling of this mixture results in the formation of four layers at some temperatures. These consist of a small and colourless petroleum layer, then a large layer of petroleum and nicotine, and below these in order a colourless, aqueous layer and at the bottom a concentrated nicotine layer. These layers, however, were clearly metastable, and on mixing gave two stable layers only.

3. Initial proportions by volume of constituents at 15°

Petroleum	60·0
Water	33·3
Nicotine	6·7

At 5°, the proportions of the two layers formed were

Petroleum layer	60
Aqueous-nicotine layer ...	40

Somewhat similar results were obtained with this mixture; the lower aqueous layer becomes cloudy at 76°, and follows the same procedure as in the preceding mixtures.

It will be noticed that at some concentrations the foregoing mixtures of liquids form two layers only, which, within a limited range of temperature, yield three-layer systems, proving how close is the relationship of the molecular volumes of the several liquids to that required by theory for partial miscibility.

These results prove that our theoretical deductions have some foundation in fact, and that with further knowledge of molecular weights in the liquid state it may be possible to predict a three-layer system in ternary mixtures as readily as a two-layer system in the case of binary mixtures of liquids.

The following results were obtained in the three-component system petroleum–nitrobenzene–water:

1. Initial proportions by volume of constituents at 15°

Petroleum	33·3
Water	33·3
Nitrobenzene ...	33·3

On vigorously shaking these liquids at 5°, three layers separate in the approximate proportions

Petroleum layer	25
Water layer	32
Nitrobenzene layer	43

. Both top and bottom layers are tinged yellow, proving that petroleum and nitrobenzene are mutually miscible to some extent. On heating to 90° and again mixing, the nitrobenzene dissolves in the petroleum and two layers are formed, the lower of which is practically colourless. On cooling, the nitrobenzene commences to separate from the petroleum at 18°, and at first takes up the middle position, but finally falls to the bottom at about 15°, when the mixture assumes its original condition of equilibrium.

2. When these liquids are mixed in the relative proportions

Petroleum	6·7	and	Petroleum	60·0	and are vigorously
Water	33·3		Water	33·3	
Nitrobenzene	60·0		Nitrobenzene	6·7	

shaken, two layers only are formed, and in each case the upper layer, consisting of petroleum and nitrobenzene, has twice the volume of the lower aqueous layer. No apparent change occurs on heating to 100°.

We have no knowledge at present regarding the molecular volume of nitrobenzene in the liquid state, but, according to the law of mixtures now put forward, the results obtained above are consistent with the view that it is similarly aggregated to aniline and the primary alcohols. Its molecular volume as compared with that of water at 15° is therefore slightly less than that of *n*-amyl alcohol, namely, 5·65, with a radius of 1·78. These values agree fairly well with its relative solubility, for whereas aniline with a molecular radius of 1·71 is miscible with water in all proportions above 167°, the corresponding critical temperature of aqueous-nitrobenzene mixtures is 235° (Campetti and Delgrosso, *Mem. R. Accad. Sci., Torino*, 1911, [ii], **61**, 187). On the other hand, although both liquids are only partly miscible with the petroleum fraction at 15°, nitrobenzene is relatively more soluble than aniline and is miscible in all proportions at a much lower temperature.

Petroleum–Nitrobenzene–Glycerol Mixture.

The complexity of the glycerol molecule has been ascertained to be one-fourth of that of water, and its molecular volume in the liquid state is only slightly greater in magnitude (*loc. cit.*). The difference, however, is sufficiently great to result in glycerol and aniline being miscible in all proportions at ordinary temperatures. Nitrobenzene, with a greater molecular volume than aniline, is

only partly miscible with glycerol, so that a three-layer system is readily obtained with equal volumes of petroleum, nitrobenzene, and glycerol. At 5°, the approximate proportions of the layers are { Petroleum layer 23 / Nitrobenzene layer 42, / Glycerol layer 35 } the nitrobenzene taking the intermediate position between the petroleum and glycerol. At temperatures above 17°, two layers only are formed, due to the nitrobenzene dissolving in the petroleum.

As already stated, these investigations were of a preliminary nature, their object being to provide data for subsequent determinations of the equilibrium existing in three-layer systems of liquids. The work here described was brought to a close in 1915, and as an early return to it does not seem probable, it was thought desirable to place on record such results as had been obtained.

In conclusion, I desire to express my indebtedness to Sir J. J. Dobbie, M.A., LL.D., F.R.S., for facilities afforded me in carrying on these investigations.

THE GOVERNMENT LABORATORY.

[*Received, March 8th*, 1918.]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 21ST, 1918, AT 4.30 P.M.

Professor W. J. POPE, C.B.E., F.R.S., President, in the Chair.

The PRESIDENT announced that Professor Gilbert Thomas Morgan had been nominated by a number of Fellows as a Vice-President, in the place of Lt.-Col. Arthur Smithells.

Dr. A. J. EWINS and Professor A. G. GREEN were elected Scrutators, and the ballot was opened for the election of Officers and Council.

On the motion of Professor H. E. ARMSTRONG, the meeting agreed that the Report of Council, 1917–1918, should be taken as read. The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ending December 31st, 1917, was proposed by Sir HERBERT JACKSON, seconded by Dr. A. E. H. TUTTON, and carried.

REPORT OF COUNCIL, 1917—1918.

The Council are gratified to report a substantial increase in the number of Fellows during the past year. On December 31st, 1916, the number of Fellows was 3,198. During 1917, 162 Fellows were elected and 10 reinstated, making a gross total of 3,370. The Society has lost 39 Fellows by death, 14 have resigned, the elections of two have been declared void, and 45 have been removed under the action of Bye-law IV for non-payment of annual subscriptions. The net total number of Fellows, therefore, as at December 31st, 1917, was 3,270, showing an increase of 72. During 1916 there was a decrease in membership of 5.

It is with profound regret they report that the following have either been killed or have died of wounds received in action :—

Arthur Joseph Brearley (1913).
Bertram Haward Buttle (1910).
Norman Phillips Campbell (1913).
Edward William Lanchester Foxell (1907).
John Maxwell Heron (1908).
Maurice Kemp-Welch (1903).
Herbert King (1897).
Arthur Edwin Tate (1909).

and that the following Fellows have died :—

Andrea Angel (1905).
James Hector Barnes (1905).
William Thirlwall Bayne (1879).
Clayton Beadle (1891).
John Forbes Bell (1907).
Charles Bradshaw (1888).
George Carrington Carrington (1887).
Alexander Macomb Chance (1883).
Taylor Cook (1907).
George Stanley Cooper (1915).
John Kent Crow (1880).
William Ralph Dodd (1886).
Oliver Statham Douse (1911).
John Joseph Eastick (1881).
John Kerr Forrest (1904).
Reginald Le Neve Foster (1872).
Ernest George Hill (1896).
George Thomas Holloway (1886).
Peter MacEwan (1886).
Norman Harry John Miller (1885).
Benjamin Horatio Paul (1868).
Rufus Daniell Pullar (1882).
John Ffraid Richardson (1911).
Henry Charles Stewart-Carlile (1917).
Francis Sutton (1860).
William Henry Symons (1874).
Walter Arthur Voss (1889).
Thomas Utrick Walton (1884).
John Williams (1892).
Charles Henry Wood (1860).
Philip John Worsley (1858).

Resignations have been received from :—

Edward James Caley (1894).
Arthur Carey (1892).
Patrick Carmody (1889).
Tom Peach Colclough (1912).
Walter Bromley Cooley (1888).
Ridsdale Ellis (1912).
Alfred William Gerrard (1875).
Harry Sands Grindley (1906).
Edwin Reginald Hughes (1903).
Norton Henry Humphrys (1883).
Stanley Allen Warrington Okell (1908)
Frederick Alfred Pickworth (1913).
Alfred Oswald Ransome (1910).
William Frothingham Roach (1908).

The hearty congratulations of the Society are offered to Sir William Crookes, Past President, elected a Fellow on December 3rd, 1857, and to Mr. John Frederick Davis, elected December 17th, 1857, who have now been Fellows for over 60 years, and also to the following who have attained their jubilee as Fellows :—

	Elected.
Sir William Phipson Beale, Bart.	Dec. 5, 1867.
Professor Alexander Crum Brown.....	Dec. 5, 1867.
Mr. Facundo Joaquin Ramon Carulla	Dec. 5, 1867.
Professor Georg Lunge	Dec. 5, 1867.
Mr. Robert Rattray Tatlock	Dec. 5, 1867.
Professor Herbert McLeod	Feb. 6, 1868.

The volume of Transactions for 1917 contains 1,128 pages, of which 960 pages are occupied by 95 memoirs, the remaining 168

pages being devoted to the Obituary Notices, two lectures on special subjects, the report of the Annual General Meeting, the Presidential Address, and the Table of International Atomic Weights. The volume for the preceding year contained 103 Memoirs occupying 1,212 pages. The Journal for 1917 contains also 2,858 abstracts occupying 1,308 pages, whilst the abstracts for 1916 numbered 3,281 and occupied 1,532 pages. The diminution in the output of chemical memoirs referred to in the last report, continued throughout the year and apparently will be still more marked in the present year. It has still been possible to obtain most of the continental journals for abstraction, and, considering the circumstances, with but little delay.

The abstracts may be classified as follows :—

PART I.	Pages.	No. of Abstracts
Organic Chemistry	—	886
Physiological Chemistry	—	265
Chemistry of Vegetable Physiology and Agriculture	—	246
	724	1,397
PART II.		
General and Physical Chemistry	—	539
Inorganic Chemistry	—	290
Mineralogical Chemistry	—	90
Analytical Chemistry	—	542
	584	1,461
Total in Parts I and II	1,308	2,858

The Council has decided to award the Longstaff Medal for 1918 to Lieut.-Col. Arthur W. Crossley, C.M.G., F.R.S.

During the past year a Joint Committee, comprising representatives of the Chemical Society and the Society of Chemical Industry, has thoroughly explored the possibility of the co-operation of the two Societies in the preparation and publication of abstracts. The Council are glad to report that, as the result of the labours of the Committee, arrangements are now in force which will practically eliminate the overlap hitherto existing in the two sets of abstracts. The editors of the Journals are in touch with one another, and the periodicals coming under review for abstracting purposes are allocated according to an agreed plan.

The economies effected by this scheme of collaboration should be considerable, but still more important, in the view of the Council, is the fact that a beginning has been made in the consolidation of

the interests of the two Societies concerned. The Council feel confident that, especially from this point of view, the new arrangements will be heartily welcomed by the Fellows of the Society. It is earnestly hoped that further developments along the same lines may be found possible, and in particular that, by the joint efforts of the two Societies, the scope of the chemical abstracts published in this country may be extended, and their value correspondingly enhanced.

The two Councils have further given their provisional approval to a scheme whereby the abstracts of each Society would be obtainable, separately and at a reasonable cost, by the members of the other Society. Steps have been taken to ascertain the amount of support likely to be given to this arrangement.

In connection with the Annual Reports, it has been decided to postpone the one dealing with the progress made in Radioactivity during the year 1917 and to publish in 1919 a combined Report for 1917 and 1918. The title of the Branch "Mineralogical Chemistry" has now been changed to "Crystallography and Mineralogy," and in accordance with the announcement made last year, the Report on this Branch appearing in Volume XIV of the Annual Reports covers the years 1916 and 1917.

For the reasons stated in the letter from Sir Edward Thorpe appearing in the Transactions for 1917 (p. 1001), it was decided to reprint the Table of Atomic Weights published in 1916. Dr. Alexander Scott, Sir Edward Thorpe and Sir William A. Tilden have been appointed by the Council to form a Committee to consider and report on a scheme for the future publication of International Atomic Weights.

The usual List of Fellows was not published in 1917 owing to the necessity of economy in the use of paper; but although this is still urgent, it has been considered desirable not to postpone publication for another year.

In view of the smaller number of scientific communications which are available for reading to the Society, the Council have decided that during the present Session the proceedings at three Ordinary Meetings shall be limited to purely formal business, and that on each occasion an Informal Meeting shall immediately follow. By arranging that an Informal Meeting should take place in the evening after the Annual General Meeting, the Council hope to afford added opportunity for personal intercourse among Fellows.

Three Lectures have been arranged for the session 1917–1918. The first of these was given on December 6th by Dr. Frank L. Pyman, who lectured on "The Relation between Chemical Constitution and

Physiological Action," whilst on February 21st Professor the Hon. R. J. Strutt delivered his Lecture entitled "Recent Studies on Active Nitrogen." The Council are pleased to announce that Dr. Horace T. Brown will deliver his Lecture, "The Principles of Diffusion; their Analogies and Applications," on June 6th next. This Lecture was to have been delivered in March, 1917, but was unfortunately postponed owing to illness of the lecturer.

Fellows will remember that one of the conditions accepted by the Council in receiving the gift of £1,000 to the Research Fund from Mrs. and Miss Müller was that a lecture dealing with the relationship between Chemistry and either Botany or Mineralogy should be delivered once in every three years. The first of these Lectures, to be known as the Hugo Müller Lectures, will be given on April 18th by Sir Henry Miers, who will discourse on "The Old and the New Mineralogy."

The situation created by the orders calling up for military service all men between the ages of 18 and 22, with the exception of engineers, was referred by the Council to the General Committee of Chemical and Allied Societies, who passed the following Resolution :—

> "This Committee desires to associate itself with the Royal Society in their action concerning the calling up of Chemists holding exemption on the recommendation of the Royal Society, and would be glad to take any action which the Royal Society consider would strengthen their hands in the matter."

This resolution was forwarded to the Royal Society. The Council also addressed communications to the War Office and other Government Departments pointing out that chemists were essential to the present and future welfare of the country, and that it would be a mistaken policy to remove them from their present occupations. The General Committee also have before them the question of hastening the release of chemists from the Colours on the cessation of hostilities.

The opinion of the Council on the proposed publication of Chemical Bibliographies in the English language has been requested by a Provisional Committee dealing with this question. The Council, deeming this to be a matter on which the Chemical and Allied Societies should confer, have referred it to the General Committee.

The problem of increasing the use and scope of the Library,

more particularly on the technical side, is engaging the attention of the Council, and the matter has been referred to a Conference of the Representatives of Chemical and Allied Societies for consideration and report. It is hoped that the results of these several deliberations will be issued to Fellows in the near future.

The congratulations of The Chemical Society have been conveyed to Professor S. Hoogewerff, of The Hague, on his attaining his 70th birthday.

Professor Percy F. Frankland and Dr. Alexander Scott have again been appointed to represent the Society on the Board of Scientific Societies.

Sir William A. Tilden has accepted the invitation of the Council to represent the Society on the Court of the University of Bristol.

The number of books borrowed from the Library during 1917 was 2157, as against 1610 the previous year. The additions to the Library comprise 155 books, of which 62 were presented, 282 volumes of periodicals and 54 pamphlets, compared with 115 books, 329 volumes of periodicals and 35 pamphlets in 1916.

The accounts for the year 1917 show a balance of income over expenditure amounting to £1,652 9*s*. 11*d*. as against £1,865 19*s*. 9*d*. reported last March for the previous year. Whilst the income from all sources was £8,529 18*s*. 11*d*., and therefore greater than that for 1916 by £365 19*s*. 1*d*., the expenditure exceeded that of 1916 by £579 8*s*. 11*d*., and reached the sum of £6,877 9*s*. 0*d*. This increase in expenditure is due principally to enhanced cost of producing the various publications, expenses on account of the Journal being £4,420 19*s*. 2*d*. as against £4,074 14*s*. 0*d*. during 1916, whilst the Annual Reports cost £64 14*s*. 2*d*. more than in the previous year. Various items of administrative expenditure have brought the aggregate under this heading from £1,281 5*s*. 11*d*. to £1,472 4*s*. 5*d*., including an increase from 15 per cent. to 20 per cent. in the war bonus paid to the staff, the provision of library furniture and of a larger supply of stationery; it has also become necessary to extend the insurance policy from £12,000 to £14,500.

The compensating items of increased income are £82 10*s*. 0*d*. on account of subscriptions, £135 11*s*. 0*d*. from interest on investments, £100 17*s*. 6*d*. from the sale of publications, and £86 9*s*. 5*d*. from advertisements in the Journal, the improved dividend on the Society's capital being principally due to the purchase of War Loan with the balance from 1916.

In the Reports for the last two years it has been the practice

to indicate the effect of the War upon the size of the Journal, and this may be brought to date by the following synopsis :—

	Number of Pages.		
	Trans.	Abstr.	Total.
1914.....	2,909	2,068	4,977
1915.....	1,862	1,944	3,806
1916.....	1,368	1,532	2,900
1917.....	1,128	1,308	2,436

It thus appears that the Journal has diminished to just under one-half the pre-war standard, and it is disturbing to find that whilst the cost of printing was £3,230 6*s.* 6*d.* in 1914, the corresponding expenditure for 1917 has been £2,543 7*s.* 9*d.*, an increase of more than 50 per cent. having regard to the relative number of pages concerned. This appreciation is due to the greatly increased cost of paper and to the fact that it has been found necessary to augment the bonus paid to Messrs. Richard Clay and Sons, Limited, which is now 37½ per cent. Valuable assistance has been rendered to the Society, however, by Mr. C. F. Cross, who has recently secured an improvement in the quality of the paper upon which the Journal is printed and has advised the Council in respect of the price which should be paid for it.

One grant only has been made from the Research Fund during 1917, the disbursement being one of £10 as against £94 for 1916, £137 for 1915, and £287 for 1914. Repayments have amounted to £61, and as the dividends have increased by £73, the excess of income over expenditure amounts to £553 2*s.* 0*d.* as against £380 17*s.* 9*d.* for 1916. Early in 1917, £500 War Loan 5 per cent. Stock was purchased with the balance from the previous year, and this capital sum, together with the substantial investment recorded in the previous Report, will help to provide a considerably increased annual amount to be expended upon chemical research when circumstances permit the resumption of normal activities.

A vote of thanks to the Auditors was proposed by the Treasurer and seconded by Dr. G. Senter, Dr. C. A. Keane making acknowledgment.

Professor W. A. Bone proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year. This was seconded by Dr. H. Forster Morley and acknowledged by Mr. A. Chaston Chapman.

In presenting the Longstaff Medal to Lt.-Col. Arthur W. Crossley, the President said:

"The introduction of ethyl malonate and ethyl acetoacetate as synthetic agents for the preparation of polymethylene derivatives

BALANCE SHEET.—THE CHEMICAL SOCIETY, 31st December, 1917.

Liabilities.

	£	s.	d.	£	s.	d.
To Subscriptions received in advance	139	3	4			
	3	0	0			
				142	3	4
,, Sundry Creditors				723	0	7
,, Research Fund :—						
As per last Balance Sheet	13804	1	4			
Add Excess of Income over Expenditure for the year	553	2	0			
				14357	3	4
,, Chemical Society : Excess of Assets over Liabilities :—						
As per last Balance Sheet...	23105	17	6			
Add Excess of Income over Expenditure for the year	1652	9	11			
				24758	7	5
				£39980	14	8

Assets.

	£	s.	d.	£	s.	d.
By Investments (value when acquired):—						
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212	8	6			
£1050 London and North Western Railway 3 per cent. Debenture Stock	839	12	0			
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	1650	0	0			
£1400 India 2½ per cent. Stock	1316	1	0			
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070	2	0			
£4341 Midland Railway 2½ per cent. Preference Stock	3572	2	5			
£1200 Leeds Corporation 3 per cent. Debenture Stock	1143	1	0			
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	1460	13	6			
£1200 North British Railway 3 per cent. Debenture Stock	1033	11	0			
£700 Canada 3½ per cent. Stock, 1930/50	704	8	6			
£2100 5 per cent. War Stock }						
£1100 5 per cent. War Bonds }	3040	0	2			
(Estimated present value of Investments, £16832 2*s.* 6*d.*)				24042	0	1
,, Sundry Debtors				861	18	2
,, Subscriptions in Arrear Estimated to realise...				400	0	0
,, Insurance paid in advance				68	13	4
,, Cash at Bank—Deposit Account	500	0	0			
Less Current Account, overdrawn	271	3	2			
	228	16	10			
,, Cash in hand	22	2	11			
				250	19	9
,, Research Fund :—						
Investments (value when acquired):						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587	18	0			
£1034 Great Western Railway 2½ per cent. Debenture Stock	1049	15	11			
£1142 16*s.* New South Wales 3 per cent. Stock ...	1000	0	0			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002	16	9			
£1365 Midland Railway 2½ per cent. Debenture Stock	1010	0	9			
£806 Victoria 3 per cent. Stock	706	6	2			
£3681 11*s.* 3*d.* 5 per cent. War Stock	3497	10	1			
				13864	7	8
(Estimated present value of Research Fund Investments, £10977 5*s.*)						
,, Cash at Bank...				492	15	8
				£39980	14	8

INCOME AND EXPENDITURE ACCOUNT

Income.

	£ s. d.	£ s. d.
To Life Compositions		247 0 0
,, Admission Fees		604 0 0
,, Annual Subscriptions—		
Received in advance, on account of 1917	250 0 0	
,, during 1917 ,, ,,	4341 0 0	
,, ,, ,, ,, 1916	366 0 0	
,, ,, ,, ,, 1915 and previous	36 0 0	
	4993 0 0	
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	390 0 0	
	4603 0 0	
Add Arrears at date: 1917, £504; 1916 and previous, £554, estimated to realise as per Balance Sheet	400 0 0	
		5003 0 0
,, Lady Subscribers		7 10 0
,, Investments:—		
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock	176 13 4	
,, £1050 London and North Western Railway 3 per cent. Debenture Stock	23 12 6	
,, £1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	34 4 4	
,, £1400 India 2½ per cent. Stock	26 5 0	
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock	45 0 0	
,, £4341 Midland Railway 2½ per cent. Preference Stock	82 15 0	
,, £1200 Leeds Corporation 3 per cent. Debenture Stock	27 0 0	
,, £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	33 15 0	
,, £1200 North British Railway 3 per cent. Debenture Stock	27 0 0	
,, £700 Canada 3½ per cent. Stock 1930/50	19 13 9	
,, £3200 5 per cent. War Stock and War Bonds	122 11 3	
,, Income Tax Recovered	135 8 11	
,, Interest on Deposit Account	86 16 4	
		790 15 5
,, Publication Sales:—		
Journals	1485 19 0	
Proceedings	10 5 0	
Collective Index	54 7 5	
Library Catalogue	1 0 0	
Atomic Weight Tables	5 9	
Annual Reports on Progress of Chemistry	170 18 0	
Memorial Lectures	3 3 3	
	1725 18 5	
Less Publishers' Commission	167 13 2	
		1558 5 3
,, Proceeds of Advertisements in Journal	£308 6 3	
Less Commission	27 2 6	
		281 3 9
,, Miscellaneous Receipts		4 2 0
,, Subscriptions from other Societies		34 2 6
		£8529 18 11

I have examined the above Accounts with the Books and Vouchers of the Society, and and the Investments.

23, QUEEN VICTORIA STREET, E.C. 4.
March 4th, 1918.

W. B. KEEN,
Chartered Accountant.

FOR THE YEAR ENDED 31ST DECEMBER, 1917.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal :—						
Salary of Editor, including Indexing	620	0	0			
Salary of Sub-Editor and Assistant	250	0	0			
Editorial Postages	16	15	1			
Abstractors' Fees	308	12	2			
Printing of Journal	2543	7	9			
Banding	56	6	11			
Printing of Advertisements	104	2	7			
Wrappers and Addressing	4	9	9			
Distribution of Journal	401	2	9			
Authors' Copies	97	0	0			
Insurance of Stock	19	2	2			
				4420	19	2
„ Annual Reports on the Progress of Chemistry				435	13	0
„ Purchase of back numbers of Journal				5	18	6
„ Library Expenses :—						
Salary of Librarian and Assistant	269	18	0			
Books and Periodicals	193	10	2			
Binding	39	5	9			
				502	13	11
„ Indexing for International Catalogue				0	0	0
„ Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological				10	0	0
„ Administrative Expenses :—						
Salary of Staff	430	15	0			
War Bonus	201	11	9			
Wages (Commissionaire, Housekeeper, and Charwoman)	187	16	6			
Coal and Lighting	72	15	2			
House Expenses and Repairs	96	4	5			
Furniture	69	12	9			
Tea Expenses	27	3	6			
Insurances	32	0	6			
Accountants' Charges	21	0	0			
Commission on Recovery of Income Tax	6	15	5			
Law Costs	1	1	0			
Miscellaneous Printing	84	5	7			
Stationery	117	5	1			
Postages	77	12	2			
Miscellaneous Expenses	46	5	7			
				1472	4	5
„ Balance, being excess of Income over Expenditure carried to Balance Sheet				1652	9	11
				£3529	18	11

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved—CHARLES A. KEANE,
E. W. VOELCKER,
C. F. CROSS.

Research Fund Income and Expenditure Account for the Year ended 31st December, 1917.

Income.	£ s. d.	£ s. d.
To Dividends on:—		
£1000 North British Railway 4 per cent. No. 1 Preference Stock	30 0 0	
£4400 Metropolitan Consolidated 3½ per cent. Stock	115 10 0	
£1034 Great Western Railway 2½ per cent. Debenture Stock	19 7 8	
£1142 16s. New South Wales 3 per cent. Stock	25 14 4	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	25 5 0	
£1365 Midland Railway 2½ per cent. Debenture Stock	25 11 10	
£806 Victoria 3 per cent. Stock	18 2 8	
£3681 11s. 3d. 5 per cent. War Loan	159 4 6	
		418 16 0
(£418 8s. 6d. purchased during year 1917)		
Repayments of Research Grants		61 1 10
,, Income Tax Recovered		92 19 8
		£572 17 6

Expenditure.	£ s. d.
By Grant to H. Wren	10 0 0
,, Cheque Book	8 0
,, Commission on Recovery of Income Tax	4 13 0
,, Advertisements	4 14 6
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet	553 2 0
	£572 17 6

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

23, Queen Victoria Street, E.C.
March 4th, 1918.

Approved—CHARLES A. KEANE,
E. W. VOELCKER,
C. F. CROSS.

heralded an entirely new aspect of organic chemistry. Until some thirty years ago, almost the only closed-chain compounds which had been fundamentally studied were derived from the aromatic hydrocarbons, and the well-recognised stability of the benzene ring had led to the development of a quite specific kind of technique—a technique in which a certain roughness in chemical treatment was permissible. The investigation of the polymethylene derivatives soon showed that these substances called for much more delicate handling.

"Professor Crossley is well known to us as one of the most assiduous workers in this new field. He has contributed to the Society a large number of papers, more especially on dihydrobenzene and hexamethylene derivatives, all of which show evidence of masterly experimentation, and many of which have important bearings on the constitutions of camphor and other components of the essential oils. Much of his earlier work was carried out under conditions which left something to be desired as regards laboratory accommodation and general facilities; British chemistry owes much to men who, like Professor Crossley, have persevered and succeeded, no matter how unfavourable to original work were the conditions under which they were placed in their earlier days.

"Professor Crossley, it affords me great pleasure, in the name of the Council, to hand you the Longstaff medal for original research in chemistry. We hope that the important work upon which you are now engaged will come to an end at no distant date, and that you will then return with fresh vigour to your life-work in the service of our science."

The PRESIDENT then delivered his Address, entitled, "The Future of Pure and Applied Chemistry." Professor H. E. ARMSTRONG moved a vote of thanks to the President for his services in the Chair during the past year and for his Address, coupled with the request that he would allow the Address to be printed in the Transactions. He also expressed the hope that the Council would circulate it among both Houses of Legislature. The motion was seconded by Professor W. H. PERKIN and carried with acclamation, the PRESIDENT making acknowledgment.

The report of the Scrutators was presented, and the PRESIDENT declared that the following had been elected as Officers and Council for the ensuing year:

President.—William Jackson Pope, C.B.E., M.A., D.Sc., F.R.S.

Vice-Presidents who have filled the Office of President.—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc.,

F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Baily Dixon, M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; William Odling, M.A., M.B., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., LL.D., F.R.S.

Vice-Presidents.—Frederick George Donnan, M.A., Ph.D., F.R.S.; George Gerald Henderson, M.A., D.Sc., F.R.S.; Arthur Lapworth, D.Sc., F.R.S.; Arthur Smithells, B.Sc., F.R.S.; William Palmer Wynne, D.Sc., F.R.S.; Sydney Young, D.Sc., F.R.S.

Treasurer.—Martin Onslow Forster, D.Sc., Ph.D., F.R.S.

Secretaries.—Samuel Smiles, D.Sc.; James Charles Philip, M.A., D.Sc., Ph.D.

Foreign Secretary.—Arthur William Crossley, C.M.G., D.Sc., F.R.S.

Ordinary Members of Council.—Julian Levett Baker; Alfred Chaston Chapman; David Leonard Chapman, M.A., F.R.S.; Alexander Findlay, M.A., D.Sc., Ph.D.; Arthur Harden, D.Sc., Ph.D., F.R.S.; Thomas Anderson Henry, D.Sc.; Charles Alexander Hill, B.Sc.; James Colquhoun Irvine, D.Sc., Ph.D.; Sir Herbert Jackson, K.B.E., F.R.S.; Robert Howson Pickard, D.Sc., Ph.D., F.R.S.; Frank Lee Pyman, D.Sc., Ph.D.; Edward William Voelcker.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 21st, 1918.

By WILLIAM JACKSON POPE, C.B.E., M.A., D.Sc., LL.D., F.R.S.

The Future of Pure and Applied Chemistry.

ONE of the most pleasurable events of annual recurrence during my younger days was the Presidential Address to the Chemical Society; it was generally a carefully prepared discourse on some technical subject of which the author was a master, and always left a lasting impression on the mind of the apprentice to our science. The long list of past Presidential addresses to our Society constitutes a maturely reasoned history of the development of chemistry during the last seventy years.

For three years past pure chemical research has been dormant the whole world over, and it would be difficult for the most accomplished essayist to arrest your attention for an hour by an address on a subject of purely academic interest. Our mental point of view and our outlook upon both present and future are entirely different from those of four years ago; although the present is obscure and painful, the future gives promise of brilliant and rapid developments in natural science in general and in chemistry in particular. In this belief I venture to lay before you some reflections upon the growing recognition of the importance of our science and upon the responsibilities with which, owing to this change in public opinion, our shoulders are laden.

I have often heard the statement made by men who have grown old in the service of science that chemistry, and particularly applied organic chemistry, is a subject in which the British nation can never excel: that minute attention to detail, coupled with the power of organisation and co-operation, entails something antipathetic to the British character; the Germans, we know, have often expressed this view. The events of the last three years have sufficed to dissipate this fallacy for ever. The manner in which Great Britain, caught in the autumn of 1914 with scarcely any resources in the shape of equipment for the manufacture of fine organic chemicals, has rapidly become a larger producer of explosive, pharmaceutical, photographic, and other essential chemicals

than Germany, will remain an enigma to the historian of these present times. The obscurity which surrounds this rapidly executed operation is not diminished by the existence of difficulties which have naturally acted as inhibiting agents. This country enjoys in a greater measure than any other State a representative Government; in spite of the many advantages of such a form of Government, the fact remains that it necessarily admits of no representation of any phase of public opinion which is not loudly and insistently expressed. Science has always been in this latter position; it has been unvocative. During the first few years of the nineteenth century, Dalton enunciated the atomic theory, Thomas Young stated the undulatory theory of light, and James Watt invented the steam engine, and by these events all the amenities of human life have been revolutionised; indeed, they have exercised vastly more influence on the well-being of our race than did the Napoleonic wars. So accustomed are we, however, to routine habits of thought that most of us would probably answer, in reply to a suddenly posed question, that the battle of Trafalgar was the most pregnant event of the first quarter of the nineteenth century.

A brief moment of reflection would lead us to correct this hasty statement. Sodium was discovered by Davy in 1807, and benzene by Faraday in 1823. From sodium we obtain sodamide, the prime agent in making artificial indigo an economic possibility; the separation of benzene from coal-tar led by logical sequence to the production of Perkin's mauve and of thousands of other synthetic colouring matters, and to the manufacture from coal-tar anthracene of synthetic alizarin, the first heavy blow aimed at the position of the Turkish Empire, involving as it did the ruin of the Turkey-red or madder industry. The first practical process for making aluminium depended on the use of Davy's sodium, and with the aid of Davy's safety lamp 250,000,000 tons of coal are mined annually in this country with comparatively slight risk. Faraday's early investigations on the chemical aspects of electrolysis and his studies on magnetic induction led immediately to the invention of the dynamo, and, through Clerk Maxwell, to the introduction of wireless telegraphy; this one branch of Faraday's investigations, in point of fact, constitutes the ground-work of the whole stupendous vista of results of the general introduction of the electric current into modern life which is so familiar to us all. Cavendish's early production of nitric acid by the passage of an electric spark through air, reproduced on an enormously larger scale, is now furnishing Central Europe with the nitric acid without which no explosives could be manufactured.

The above-mentioned and multitudes of other fundamental dis-

coveries in physical and chemical science were made almost within a stone's-throw of this room; most of them were made in the Royal Institution, and all of them by an expenditure of money infinitely small as compared with their present-day effects.

Anyone who is in the habit of reading modern historical writers—and they have become quite illuminating since a scientific mode of writing history has been substituted for the older fictional style—knows how political changes, national reforms arising from an effort of the collective conscience, the magnetic influence of some popular demagogue, and the like, are invariably invoked as explanatory of all the vicissitudes of our planet.

The modern historian is here taking a false point of view, and, since he is, in general, quite unacquainted with physical science, his methods are inadequate. The whole history of Europe for the last century has been made within a few hundred yards of Burlington House in our scientific laboratories. One of the most potent incentives to political changes resides in the desire to increase the amenities of life, and research in pure science has had for a hundred years past the greatest influence in facilitating the realisation of that desire. Co-operative effort, one of the most striking aspects of modern life, only became possible when science provided the facilities for municipal power schemes, for telegraphic connexion over the whole world, and for the concentration of production in definite centres. Chemical science is still furnishing the means for further revolutionary changes; during the last few years we have seen great technical developments of purely scientific discoveries—the work of Dewar on the liquefaction of gases, and that of Cross and Bevan on viscose and artificial silk, both of which have led to the profitable utilisation of vast amounts of capital—and it is as yet impossible to indicate the ameliorations of the conditions of human life which will inevitably result from contemporary chemical investigation.

In a time of crisis like the present, British custom tends towards the replacement of unreal conventions by what is really vital; we have been engaged upon this operation for several years. Whilst previously unheard-of changes have succeeded each other kaleidoscopically in the national constitution, in the political parties in power, in the freedom of the subject, and in hosts of other ways, the nation has recognised that science is the only real maker of history. The whole Empire is now one vast chemical and engineering laboratory, and we even live on a scientific ration of so many calorific units. It is obvious that chemistry, with physics, engineering, preventive medicine, and others of the natural sciences, which previously had no imperialistic position, because powerless

to make or break a Government, have become the pivot on which turn all our hopes of retaining an independent national existence; it has been suddenly realised that supremacy in these branches of knowledge is vital to our country.

The time is approaching when this state of affairs will change; neglect of the natural sciences will then no longer put us in danger of sudden extinction, but, as was taking place years ago, will lead to our slow, certain downfall as a nation. The responsibility is placed upon our scientific men of taking such measures as will ensure that the old order is not re-established, that science makes her voice heard in our national councils, and that policies of drift are for ever abandoned.

We have in this country three large and long-established organisations devoted to various phases of chemical science: the Chemical Society, the Society of Chemical Industry, and the Institute of Chemistry. Is it too much to ask that these three representative bodies, with perhaps the newly-founded Association of British Chemical Manufacturers, and ultimately all the other cognate but more specialised interests, should set up a watchful and alert joint Council with directions to consider national questions in which any of the varied interests of chemistry are concerned, and to make such representations to our administrators as would voice the corporate view of the joint body.

I am inclined to think that, had such a body been in existence several years ago, much that has been accomplished in the interval by somewhat devious methods would have been better done. One instance will occur to everyone: that of the much-debated question of the re-establishment of the coal-tar colour industry in Great Britain. The scheme adopted by the Government for resuscitating this phœnix in our country, after its past thirty years of profligate productivity on the Continent, was launched without scientific advice; the Cabinet mouth-piece, indeed, declared that the directorate of the company was not to include men of scientific knowledge, on the ground that a director who knew something about the business of the company would have an advantage over his less well-informed colleagues.

Owing largely to the fact that we possess no strong collective council, representing the combined academic, scientific, and industrial aspects of our science and capable of representing them before a representative Government, it may be argued that we chemists are not altogether blameless for the particularly blundering way in which particular errors have been perpetrated by the responsible officials. Whilst we should be thankful that our blunders have not led to our destruction, we should proceed without further

delay so to organise the resources of chemistry as to make it possible to enforce the adoption of scientific methods and modes of thought by authorities to whom these are yet strange.

The serious character of the British position in connexion with the coal-tar colour industry becomes more evident when one considers that this is a key industry; upon it depend the textile, paper, photographic, and pharmaceutical industries. The total capital employed in the organic dye industry in Great Britain is between four and five million pounds, whilst the capitalisation of the German coal-tar colour firms is of the order of fifty million pounds. The need for greater and more intelligent activity in this direction is obvious; unless national enterprise can be stimulated into providing adequately for the manifold requirements of Great Britain and her Colonies in all those industries which depend on coal-tar colour manufacture, we shall be again in the hands of the foreign producer.

The control of a national dye scheme by business men with no real feeling for the enterprise on which they are engaged renders it fairly certain that the wider aspects of coal-tar colour manufacture will be neglected. The interweaving of the colour interests with those of synthetic pharmaceutical, photographic, and other chemical industries is essential to success. The utilisation and development of the resources of the Empire in natural colouring matters such as indigo is necessary from a national point of view. The careful study of our own and other codes of Patent Law in their bearings upon the fine chemical industry is also important. These weighty questions cannot receive adequate consideration from any purely lay body.

It is mournful but instructive to compare our present position in the coal-tar colour industry with the prospects which that branch of applied chemistry exhibited to Great Britain in early days. The first coal-tar colour was made by Perkin in 1856, and in 1862 Professor A. W. von Hofmann, one of the foremost chemists of the day, a German, domiciled in this country, painted an alluring picture of the future in store for us. Said he: "England will, beyond question, at no distant day, become herself the greatest colour-producing country in the world, nay, by the strangest of revolutions, she may, ere long, send her coal-derived blues to indigo-growing India, her tar-distilled crimsons to cochineal-producing Mexico, etc." When we contrast this dazzling prospect, made by one of the most far-sighted of contemporary German chemists, with the actual situation, we cannot but ask why the event fell so miserably behind the forecast. The reason, in my opinion, lies in the fact that opulent, indolent Great Britain has

for the past century permitted all its educational interests to pass into the hands of a particular caste which despises all knowledge difficult to attain and, to camouflage its own idleness, has always pressed the notion that a first-hand knowledge of the facts of natural science and the conclusions to be drawn therefrom is unimportant, and that the young man or young woman does his or her best in the world if thrown into it entirely destitute of anything but an evanescent acquaintance with certain classics and a decided taste for so-called learned leisure. The greater among the ancients were creators of new knowledge as well as masters of the whole accumulated world's stock of information; their successors, unproductive of positive knowledge and very ignorant of the great changes taking place around them, can but wonder at and comment vaguely on the genius of Archimedes and Aristotle, and necessarily despise the achievements of Newton and Kelvin, their modern prototypes. Illustrations of the stultifying effect of a purely classical education are laid before us every day; one recent example may be quoted here. The gentleman who shares with Mr. A. J. Balfour the honour of representing in Parliament the greatest centre of business and financial activity in the world made the following statement in the House of Commons last Thursday whilst opposing Mr. Fisher's Education Bill: "It was said that education was necessary to make the rising generation good business men. His experience in the City was that the man who took Firsts at Oxford generally came out last, and that the man who could hardly write his name generally came out first. The explanation was that education could not put into a man that instinct of self-preservation and common sense which was the foundation of all success in business. How could education assist a farm labourer to spread manure on a field? The best labourer he had known was wholly illiterate. If the waste of the war was to be replaced it would be necessary for the young to start as early as possible in doing a day's work, instead of wasting time on useless book learning." This representative of the City of London is a baronet of recent creation and a director of one of the largest London banks and of one of the most important English railroads; he received his "education" at one of the oldest and most rigidly classical of our great public schools. Comment is probably unnecessary.

Every scientific man in the world realises that an innate appreciation for fine literature, for great thoughts nobly expressed, and for the appropriate delineation of our greatest aspirations, are among the most sublime instincts of humanity and demand the most careful cultivation. Our literary men say that we cannot

express ourselves effectively, and offer as a satisfying feast the old bones left us by the Greeks and Latins, chewed over for centuries until so devoid of nutriment that they led ultimately to the mental atrophy which characterised the Middle Ages, an atrophy that was only shaken off by the taste for knowledge which arose from the exploits of geographical science in the Elizabethan period.

If the power of expression rests with our literary friends, why are they so idle? It is their obvious duty to devote themselves to popularising the natural knowledge acquired by the scientific observers of the past two centuries; this real learning has so infinitely extended human interest in the world around us and gives such promise of further conquests that an appeal for its consideration would certainly not have been made in vain to Plato or Lucretius. No one asks for the abolition of classical literary learning, but the whole world is now demanding that the young should be provided with an education which includes an insight into our present-day knowledge of the universe.

The rather petty disputes which rage about this matter of classical and scientific education are one-sided; the scientific man generally knows something of both aspects of the subject, whilst his classical compeer rarely has any acquaintance with science. Unfortunately, the great questions involved have more than a petty bearing upon the well-being of our nation. The classical school has held our country in such bondage that, to all practical intent, no person can be admitted to the higher public service unless he swear adhesion to the caste. It is almost regarded as a platitude that acquaintance with natural science disables a man from fulfilling any high public office; practically all the superior positions in the Civil and Diplomatic Services must be filled by men of classical instincts.

I venture to think that the wisdom of this mode of selection has been seriously impugned during the last four years. The huge Government departments which have arisen of late may be divided roughly into two classes—those staffed by men of some scientific training and those staffed by classical university graduates. Anyone who has had occasion to note the numerous recent criticisms on Government departments must have observed that these strictures have almost invariably been passed on administrative branches of the service; delay, the encumbrance of red-tape and inability to draw a decision, seem indigenous in certain Government offices, and none of the numerous attempts at reform has been successful. The administrative services are those in which the classical man is predominant. Other branches, such as the home Army Medical Service, have practically never been charged

with inefficiency; the worst that has been alleged is a suggestion of extravagance.

The department just named is staffed by men who have had, at least, the rudiments of a scientific education; if control in the Royal Army Medical Service had been vested in the classical scholar of ability but no knowledge, it is certain that the last three years would have seen a repetition of the horrors of the Crimean campaign and that the army mortality from disease would have been greater than that caused by the ordinary instruments of war.

Such a control, happily, has been avoided; it has been avoided merely because medicine possesses the collective organisation for which I plead in chemistry, an organisation so strong as to make the imposition of an irresponsible lay control unthinkable.

I have already directed attention to the frequently expressed opinion that, as a nation, we are incapable of excelling in the fine organic chemical industry; let me quote one instance, small in itself, but large in its consequences, in disproof of this view.

The ordinary photographic plate is sensitive only to a region in the blue of the spectrum, but by incorporating certain rather fugitive organic dyes with the sensitive film, the latter may be rendered sensitive to the green, yellow, and red parts of the spectrum; photographic plates so treated are described as panchromatic. The quantities of the sensitising dyes required for the whole world's consumption in normal times is minute, being, indeed, of the order of a few pounds per annum. Until 1915, these substances had never been made outside Central Europe, and little was known by us of their compositions or of the methods of preparing them, as they were all sold under trade names. The manufacture of these materials, small as was the whole business, had been industriously cultivated by the German colour works, and, as these colour sensitisers are essential in aerial photography, their scarcity became of serious import quite early in the war.

The experimental investigation of the whole subject was quickly put in hand in this country, and within a few months ample supplies of the usual sensitisers were produced. Further, the newly established Department of Scientific and Industrial Research financed the development of the study of photographic sensitisers; as a result of this action, new sensitising dyes have been produced which are far superior to the older ones. It is safe to assert that the manufacture of panchromatic plates has now attained a degree of perfection in this country such as will long defy competition.

This is but one case that may be quoted from among a host of others, all of which prove conclusively that, given a little encourage-

ment and assistance, British chemistry is capable, not only of giving much-needed relief in this time of strain, but of meeting every demand which can be made on it when the period of reconstruction commences.

Whilst the absence of the powerful weapon provided by a collective chemical Council, embracing all interests of the science, has made it impossible for us to render the most economical service to our country, it is perhaps satisfactory to reflect that hitherto all that has been sacrificed is economy. Our lack of power to enforce our views has led to financial extravagance on the part of the authorities; the lack of economy in time, which means lives, cannot be attributed to our chemists. The duty will fall to some future President at some later time to record the spontaneity with which the Fellows of this Society volunteered for service in our chemical works, our munition factories, and with the Colours either in our gas service or elsewhere.

One aspect of this question, however, calls loudly for attention. For several years past our teaching staffs have been depleted, and but a small fraction of the normal number of young men have been able to present themselves for training in chemistry. Whilst the present demand for capable young chemists is vastly in excess of the supply, an even more serious situation awaits us in the future. If hostilities were to cease to-morrow, five years would be needed before our colleges and universities could begin to supply the large numbers of young chemists which will be required for the development of the future great fine chemical industry of this country.

Surely this is a matter which should engage the serious attention of the country. If it prove necessary to import young chemists from neutral nations to man our reconstruction schemes a handicap will be established which we may never outrun. The adoption of some scheme by which a sufficient number of juniors can be provided to help in the great developments which the future has in store for the scientific industries of the country is of the utmost importance.

It is impossible to reflect on the desirability of a closer co-operation between the large societies representing chemistry in Great Britain without foreseeing many directions in which such a union would be of value. As in every time of awakening, there exists at present a great feeling of unrest among the younger members of our profession; of late quite a number of propositions for the formation of new scientific societies have been promulgated, and all for the purpose of placing more power in younger hands and for ensuring to the juniors more security of advancement. The final objects of these propositions, so far as I have understood them, are

entirely praiseworthy, but it is to be feared that the methods suggested for their attainment are not always such as appeal to older and more experienced people as likely to prove successful. If we chemists collectively were in possession of some more centralised organisation, such an one, for example, as is represented by the Chemists' Club in New York, with facilities for hospitality, meetings, library, laboratory accommodation, and the like, no question could ever arise of the creation of a new chemical body unconnected with the main organisation. A new and vigorous issue of the parent organisation would shoot at appropriate intervals, and would remain contributing to the strength of the family under the original patriarchal roof. We greatly need a central home of all the chemical interests in the country, and premises several times as large as the Chemical Society rooms, to use as a club, of which every chemist in the country would be a member. The question of the necessary expansion of the Library, which is occupying the earnest attention of your Council, would find an easy solution in such a pooling of interests.

Notwithstanding that, during the past forty years, much has been done to facilitate the entrance of talented and promising young men into the scientific professions, far more progress must be made in this direction if we are to regain for Great Britain the paramount position she once held in scientific discovery. The Natural Science Departments in every University in the country call for expansion in personnel, laboratory space, and equipment, and in provision for post-graduate research work; whilst scholarships for students in training are fairly plentiful, the difficulties which face the advanced student who needs to spend, and who would benefit immensely by spending, several years on original research, are often insurmountable. Every professor of chemistry in the country can recall many instances in which he has had to send his students into technical life at too early a period, simply because it has been impossible to secure for a good man the £150 or £200 per annum necessary for living expenses; the provision of this small sum would, in many cases, convert a half-trained chemist into a far greater asset to the State.

Whilst a collective effort, exerted by all the interested branches of our science, to ensure the efficiency of the newly-established organisations for furnishing the requisite relief, is urgently desirable, it should be noted that it will become increasingly difficult to retain students capable of taking leading positions for a sufficient time to ensure their proper training. During several years past I have been visited by gentlemen representing large chemical industries who have walked round my research labora-

tories to sort out the workers and to make overtures to such as they judged suitable for their own work; the pressure thus exerted upon the universities to force the premature delivery to the works of the best men they have in training will necessarily increase with the coming still greater demand for technical chemists.

The intellectual professions may be roughly classified in two categories: the productive and the parasitic. Those of the productive class, which includes all scientific workers who produce new knowledge, are, in general, poorly remunerated; their practitioners are ordinarily so intensely held by the interest of the work in hand that they have little inclination to divert their energies to the necessary extraction of higher emoluments. The parasitic class, on the other hand, have always been able to command ample remuneration for their labours; the reasons for this difference are various, and need not now be detailed. It may be noted, however, that at the jubilee of this Society in 1891 the veteran, Sir W. R. Grove, who in his young days did so much to develop chemical science, told us that he was led very reluctantly to desert chemistry for the Law because "the necessities of a then large family gradually forced me to follow a more lucrative pursuit." The autobiography of the late Lord Playfair tells a precisely similar tale. Neither of these men is now remembered by anything beyond the great achievements in chemical science of his early days.

The fact emerges that if science is to remain in its service such a proportion of the most powerful intellectual and creative talent of the Empire as will suffice for our progress as a nation, some method must be devised for securing to its followers appropriate emoluments commensurate with those now allocated to the non-productive professions.

This is not only necessary in connexion with those purely utilitarian branches of chemical science to which I have already directed attention, perhaps too insistently, for illustrative purposes. A great danger exists at present, and will grow in the future, that the enormous productiveness of experimental science will overshadow the importance of scientific work of less immediate utility. It would be a great calamity if pure science were neglected in favour of the cultivation only of natural knowledge which gave immediate promise of beneficial material results. One of the most important functions of any expression of collective chemical interests such as I have foreshadowed would be to ensure that pure unproductive scientific research should be retained on an even higher level than that assigned to immediately productive original investigation.

At the present time, physics and chemistry are merging into

one; we foresee that the near future will furnish us with still broader views of the universe and will mark a new development more illuminating even than the great advances which followed Dalton's atomic theory and all its nineteenth century sequences. No material interests must be allowed to check this stupendous expansion of our knowledge.

OBITUARY NOTICES.

ARTHUR JOSEPH BREARLEY.

Born April 1, 1890; Killed in Action June 20th, 1917.

Captain A. J. Brearley, of the Devonshire Regiment, attached Special Brigade Royal Engineers, was reported killed in action on June 20th, 1917. Captain Brearley was a native of Birmingham, being the elder son of Mr. and Mrs. Brearley, of Small Heath, Birmingham. He was educated at King Edward's School, Camp Hill, and the High School, Birmingham, where he obtained several scholarships. He proceeded to Cambridge in 1909, where he was a scholar of Emmanuel College. In 1912 he graduated, having obtained a First Class in Part I. of the Natural Science Tripos and a Second Class in Part II. of the same Tripos. During his university career he rowed and obtained his second May colours.

Prior to the war he was science master at Exeter School. He was granted a commission in April, 1914, being promoted lieutenant in February, 1915, and captain in June of that year. He was transferred to the Royal Engineers in July, 1916, and proceeded to the front in April last year.

His brother, Sec.-Lieut. Norman Blackburn Brearley, Royal Warwickshire Regiment, was killed in action in Mesopotamia in April last year. The only surviving child, Lieut. Selwyn Blackburn Brearley, is serving with the Devonshire Regiment. Captain Brearley was twenty-seven years of age.

BERTRAM HAWARD BUTTLE.

Born March 20th, 1888; Died October 1st, 1917.

By the death from wounds of Bertram Haward Buttle, the Chemical Society has lost one of its younger workers from whom

much might have been expected in the future, whilst those who knew him personally have lost a dear friend for whom they had the greatest respect as well as affection.

Buttle, when first I knew him, was a boy in the former People's Palace Technical Schools. After a short interval at West Ham Polytechnic, he returned to East London College and took the Science Course, graduating with Honours in Chemistry at the B.Sc. examination in 1907. After taking his degree, he went on with post-graduate work, the results appearing in the *Transactions*.*

He took up teaching, and was Science Master at Archbishop Holgate's School, York, when Professor Meldola asked me if I could recommend anyone for a demonstratorship at Finsbury Technical College. Knowing that they both possessed a common characteristic, absolute scientific truthfulness, Buttle seemed the right man, and, as might have been expected, fully justified the choice.

Almost immediately after the outbreak of war, Buttle joined the University and Public Schools Section of the Royal Fusiliers, but was drafted for service in France with the Gas Section of the Royal Engineers in July, 1915. After service with the Mediterranean Expeditionary Force in the winter of 1915—16, he returned to England, obtained his commission in May, 1916, and was in France and Belgium until last autumn, when he was wounded by an aeroplane bomb and died in hospital an hour later.

The letters of sympathy received by his parents give an idea of the impression Buttle gave of his character to those who knew him. The Rev. W. Johnson, formerly headmaster of Archbishop Holgate's School, wrote: "He was such a real man, so thorough and sincere that he gained everybody's affection in my school, both staff and boys. It is rare to find such wisdom with goodness in so young a man, and much as I felt it his advantage to leave me, I mourned his departure from my staff as that of a dear friend.

"His sense of duty was very high and his influence on my boys most excellent."

Major Monier-Williams wrote: "His death is a great grief to me, personally, as I was very much attached to him. He had been with me for several weeks and had always shown the greatest keenness and interest in his work. He was extraordinarily cheerful and willing, and nothing ever seemed to be too much trouble for him. I could always be certain that whatever I gave him to do would be well and thoroughly done."

Captain Bansell referred to the time Buttle served in his com-

* "Solubility of silver chloride in mercuric nitrate solution," 1908, **93**, 1405.

"Constitution of polynitrophenols in alkaline solutions," 1909, **95**, 1775.

pany, "where his courage and never-failing good spirits won him the love and esteem of all officers and men with whom he came in contact."

Such was Buttle, honest, industrious, keen on his work, and always cheerful and ready to do a kind action. Personally, I recall the many pleasant days spent working together. His friends mourn his loss deeply. J. T. Hewitt.

NORMAN PHILLIPS CAMPBELL.

Born April 25th, 1886; Killed in Action May 3rd, 1917.

Norman Phillips Campbell was the son of Mr. James Campbell, of Montreal, and was born in Chicago on April 25th, 1886. He received his early education at the High School, Montreal, at Cliftonville, Canada, and Dulwich College.

He entered Balliol College, Oxford, in 1904, taking his degree in 1907 and becoming M.A. in 1913. Specialising in physical chemistry, he published in collaboration with Hartley papers in this journal on the solubility of iodine in water (T., 1908, **93**, 741), and a new apparatus for preparing conductivity water (*ibid.*, 428). In 1908 he decided to go to Ceylon to take up a post under the Church Missionary Society at Trinity College, Kandy, one of the largest secondary schools in the colony. On the outward voyage he carried out an investigation of the salinity of the Indian Ocean with the aid of Manley's differential densimeter, the results being subsequently published in the *Proceedings of the Royal Society of Edinburgh* (**33**, 124).

Campbell worked in Kandy from October, 1908, until the end of 1914. Although his teaching and duties as a social worker amongst his pupils (which entered very largely into his life) left him little time for research work, he carried out an investigation on the rate of crystal growth, which was published in the *Transactions* for 1915 (T., 1915, **107**, 475).

In December, 1914, he returned to England and enlisted as a private in the London Scottish, shortly afterwards obtaining a commission in the Oxfordshire and Buckinghamshire Light Infantry, and transferring to the Royal Engineers Special Brigade when it was formed. He was wounded at Loos in 1915, but was soon able to return to duty. In May, 1916, he was promoted Temporary Captain; he was killed in action on May 3rd, 1917, leaving his wife and two young children. His many friends have

cause to lament the death of a man of conspicuous ability and of singular nobility of character, whose death for his country was typical of his life of devotion to others and to his duty.

A. F. J.

EDWARD WILLIAM LANCHESTER FOXELL.

BORN JULY 7TH, 1884; DIED JUNE 11TH, 1917.

EDWARD WILLIAM LANCHESTER FOXELL was the third son of the Rev. W. J. Foxell, Rector of St. Swithin's, E.C. He graduated in science at University College, London, under Sir William Ramsay, and was appointed in 1907 a Master in the Science School and Junior House Master in Christ's Hospital. For many years he was an officer in the O.T.C., becoming O.C. on Colonel Boardman's departure for active service. In Christmas, 1914, he resigned the O.T.C. and was gazetted Captain in the Buffs. During service at the front he fell ill with trench-fever, and died in France of appendicitis on June 11th, 1917.

Those who were so fortunate as to know Mr. Foxell intimately recognised in him a man of versatile attainments. He had a profound appreciation of all that is beautiful, whether in art, literature, or music.

MAURICE KEMP-WELCH.

BORN 1880; KILLED IN ACTION APRIL 11TH, 1917.

MAURICE KEMP-WELCH was born at Bristol in 1880. He was educated at Clifton College and King's College, Cambridge, taking the Natural Science Tripos in 1903. He was an honorary scholar of his College.

On leaving Cambridge, he entered business life, dealing with the commercial chemistry of oils, in which he was greatly interested. He conducted a number of important experiments on wood-oil.

Immediately after the outbreak of war he applied himself to adapting German methods in rubber, and with Mr. Hadfield devised a process of coating canvas with rubber which promised well for the future. Although his concern with these devices was in the first instance commercial, the one characteristic he always showed was science for science' sake. He was on the eve of perfect-

ing some interesting researches in oils when he obeyed his country's call.

He enlisted in November, 1915, in the O.T.C. at Lincoln's Inn. He went to France with the 10th Batt. Yorkshire Regiment in June, 1916, and fought through the battles of the Somme. He was killed on April 11th near Henin-sur-Cojeuil.

Those who knew of his scientific work regret that his ingenuity, which had just begun to produce valuable results, should now be permanently lost.

He married in 1911, and leaves a widow and one daughter.

HERBERT KING.

Born April 7th, 1876; Killed in Action October 6th, 1917.

Herbert King was born in Scarborough in 1876, in which town he received his early education, winning a scholarship to St. Martin's Grammar School, and three years later a County Major Scholarship to the Yorkshire College, the present Leeds University. After a course of three years at the Yorkshire College, he graduated in 1895 as B.Sc. with Honours in Chemistry, and also won the Senior Ackroyd Scholarship, which, however, he resigned in order to take up a teaching post at St. Martin's Grammar School, Scarborough.

He was elected a Fellow of the Chemical Society in 1897. In 1895 he became an Associate of the Institute of Chemistry, and in 1900 was elected to the Fellowship with a special diploma in pharmacology, toxicology, and microscopy. In 1901 he became a M.Sc. (Victoria), and in 1905 a M.Sc. of Leeds University.

He was a member of the Priestley Club and also of the Standing Committee of Convocation of the University of Leeds, the chairmanship of which he resigned on joining his Majesty's Forces in February, 1917.

Between 1897 and 1908 Mr. King held posts as Science Master at Dronfield Grammar School, Sheffield, Ashville College, Harrogate, Wolverhampton Grammar School, and Scarborough Municipal Secondary School. In 1908 he was appointed Head of the Chemical Department of the Cockburn High School and Technical School, Leeds, which post he held to the time of his entering the Army.

From 1909 to the time of his death he was the Public Analyst for Scarborough.

In February, 1917, Mr. King was gazetted to a commission in

the Army Ordnance Department, and after undergoing training in a special course at Woolwich, he was engaged on Government work at Portsmouth, from whence he proceeded to France in August, 1917, and was killed by an enemy bomb on October 6th of the same year.

A. J. C.

LEONARD ISON PITT.

BORN 1888; KILLED IN ACTION JULY 30TH, 1915.

A PROMISING life was cut short by the death in action of Leonard Ison Pitt. Pitt received his early education at the Coopers' Company's School, matriculated at an early age, entered East London College in 1904, and took the Final B.Sc. (London) examination in 1908 with First Class Honours in Chemistry, a month or two after his twentieth birthday.

The next year was spent at research work, which was interrupted when Pitt went to Stamford Grammar School as Science Master in 1909; at the time of the outbreak of war he was assistant head at the school. During this period, he took a great interest in agriculture and agricultural chemistry, and passed the first part of the Diploma of Agriculture at Cambridge.

After reading the above record, one might imagine that Pitt's twenty-six years of life up to 1914 had been spent entirely at work. As a matter of fact, he was a very keen sportsman, and especially excelled at football, whilst he took a considerable part in the social life of his college, endearing himself to all who knew him. Pitt was very much alive, and with his witty sayings and pleasing personality kept his immediate neighbours lively as well, whether on the football field or in the research laboratory.

He enlisted at the outbreak of war in the 8th Battalion of the Rifle Brigade, and was very proud of being one of the First Hundred Thousand of Kitchener's Army. By dint of hard work and his power of commanding men, he obtained rapid promotion and became platoon sergeant of "D" Company before many months had elapsed. He embarked for France in May, 1915, and met his death at Hooge while leading his platoon in a counter-attack on July 30th, 1915. The Officer Commanding his platoon writes:

"A better Sergeant or friend no man could wish—he met his death as only an English gentleman can—leading an attack against great odds."

A man of Pitt's great ability and many attainments naturally

had a large circle of friends, who, whilst lamenting his death, love and respect his memory. J. T. Hewitt.

ARTHUR EDWIN TATE.

Died April 22nd, 1918.

Arthur Edwin Tate in 1898 entered the Durham College of Science, now Armstrong College, in the University of Durham, Newcastle-upon-Tyne, as a student in the Education Department. He graduated as Bachelor of Science in 1901, with chemistry as a principal subject. His interest in chemistry was real and living, and led him to devote his spare time to further work in this subject. While teaching in the neighbourhood of Newcastle, he worked in the College laboratories in the evenings and Saturdays, and after his appointment to the science mastership at Pontefract Grammar School he continued the experimental investigations thus begun. In 1909 he submitted the results of this work for the M.Sc., and was awarded the degree. In 1910 he was appointed senior science master of the City of Norwich School, a position which he filled with marked success. He joined the Royal Engineers in July, 1916, and went to France in the following September, where he was wounded on April 12th, 1917, and died from the effects of his wounds ten days later. Arthur E. Tate was a man of sterling qualities, a good and successful teacher. He leaves a widow, to whom he was married shortly before he joined the Army.

P. P. B.

CLAYTON BEADLE.

Born 1868; Died August 16th, 1917.

Clayton Beadle died at his residence at Sidcup on August 16th, 1917, at the age of forty-nine.

Mr. Beadle had been seriously ill for some time, but recovered sufficiently to undertake a long foreign tour, partly on business and partly for recuperation. Although for a time able to resume his professional duties, he was unfortunately, after a brave struggle, again laid low, and ultimately succumbed.

Clayton Beadle commenced his chemical career at the works of his cousin, Mr. Edmund Joynson, the well-known paper maker,

where he studied under Messrs. Cross and Bevan, and formed with them a lifelong friendship. After some time he became a partner in that firm, and during that period he was associated with the various industrial developments of cellulose xanthate or viscose, the name by which it is industrially known.

On the termination of the partnership, Mr. Beadle associated himself with Dr. Stevens, and with him practised as an analytical and consulting chemist. He was not only an expert in the science of paper-making, but was an acknowledged authority on matters connected with the chemistry of rubber, with which branch of industry he was intimately connected.

He also did good work in conserving the water supply of the Kent district. In this connexion, it is interesting to note that his father, Mr. Charles Beadle, gave valuable assistance to the Commission appointed to consider the condition of the lower reaches of the Thames.

Mr. Beadle made numerous contributions to technical literature, and his work was recognised by various societies, including the Royal Society of Arts, La Société d'Encouragement pour l'Industrie National (Paris), and the Franklin Institute (Philadelphia).

ALEXANDER MACOMB CHANCE.

BORN JUNE 28TH, 1844; DIED NOVEMBER 22ND, 1917.

ALEXANDER MACOMB CHANCE, J.P., was the ninth and youngest child of George Chance, of Birmingham, brother of the founders of the well-known firm of Chance Brothers & Co., of Spon Lane and Oldbury. His mother was Cornelia Maria, daughter of Arent Schuyler De Peyster, of New York, in which city George Chance lived for many years as partner with his brother William in trade with the United States.

Alexander Chance was born on June 28th, 1844, after his father's return to England. Having completed his education at Lausanne, he found employment with his relatives at their glass works at Spon Lane. The capacity that he showed soon gained for him, in 1868, the managing direction of their alkali works at Oldbury. In 1879 he was admitted a partner in the firm, and he retained the principal direction of the works, from 1901 as Chairman of the new firm of Chance & Hunt, Limited, until his retirement in June, 1912.

From the start he showed of what metal he was made. Much

wanted doing, and he did it, speedily restoring prosperity to the works and enhancing it as years went on. He was not a man of science; as he himself wrote at the beginning: "I frankly admit that my predisposition is decidedly in favour of commercial negotiations, etc., rather than of the technicalities of manufacture." He was an organiser, a director of industry, able to get the best out of his skilled subordinates by animating them with his own energy and zeal. As has been said of a modern French general, "he radiated vitality." He was ever watchful of all improvements, of new processes, of all means by which production might be increased or losses saved. Of his many successes need only be noticed here his great triumph, the Chance Sulphur Recovery Process. If he did not himself work out the chemistry of this, he directed the experiments and faced the expenditure, and in that sense may be said to have been truly the inventor of it.

Prominent among his characteristics were a singular power of quick and correct decision and a discerning knowledge of men. Those whom he gathered round him in the office, in the laboratory, and in the works formed a staff difficult to match. He treated them as friends rather than as servants, and similarly with the workmen it would be hard to find a master enjoying to a greater degree their goodwill and affection.

In social work for their benefit he was indefatigable. Institutions established at Oldbury before his time, schools, dispensary fund, mission, and relief work, he sedulously fostered, and much else he initiated or promoted, amongst them being religious endeavours, mutual help, sanitary housing, and temperance. The drunkenness that had been rampant at the works he abolished, himself taking the pledge, to the detriment of his health, to set an example. An early achievement was the Convalescent Home at Quinton, a few miles from the works, supported and managed by the men themselves, and regarded by them as their own. Other benefits to them were the Temperance Club and Institute at Langley, and the Provident Accident Fund, which he devised on the passing of the Employers' Liability Act. That Act, he saw, would cover but very few accidents, would involve long delays in its operation, and would be a fertile source of friction between masters and men. Under his scheme, the firm contributed equally with the men to a fund from which the compensation adjudged for each case was paid without question of whose fault, and instantly. One result, not perhaps foreseen, was an extraordinary diminution in the number of accidents. Undoubtedly a sense of personal interest made the men more careful.

These philanthropic activities were by no means limited to Oldbury. Alexander Chance associated himself actively with almost every movement for social advance in Birmingham and its neighbourhood. The cause of temperance found in him an unwearied protagonist. Generous to a fault himself, and giving for the love of it, he had a singular ability of persuading others to give also, and largely. If any fund of importance were to be raised, it became habitual to enlist him early in the cause. It may be questioned whether the money for the Birmingham bishopric could have been raised without his persuasive pressure on rich men. The Birmingham Young Men's Christian Association owes its great modern development and success largely to his efforts. His "St. Andrew's Guild," a work for which he received the thanks in writing of four bishops, transformed one of the worst slum parishes of Birmingham into a model of church organisation and life. His last achievement, pursued to a successful end through years of discouragement, was the acquisition of Warley Park for the use and enjoyment of the public.

His married life was of uniform felicity. His first wife was Florence, daughter of Major Arthur H. H. Mercer, 60th Rifles; his second, Agnes Elizabeth, daughter of William Fleming, of Inverness. Both entered zealously into all his social and philanthropic work. By the former, who died in 1903, he had eight children, of whom four sons and a daughter survive him. His last years he spent in quiet retirement at Torquay, where he died, worn out with work, on November 22nd, 1917.

JOHN JOSEPH EASTICK.

BORN FEBRUARY 6TH, 1855; DIED SEPTEMBER 7TH, 1917.

JOHN JOSEPH EASTICK was born at Great Yarmouth, and in early life had his attention directed to industrial chemistry, his father being manager of the Southtown Gas Works there, and afterwards at Peel, Isle of Man. Before coming to Lancashire and taking up the systematic study of science, he had assimilated the contents of Clegg's "Gas Manufacture," and often took the keenest delight in giving his interested fellow-students an outline of the various operations in the manufacture. The early impressions thus gained lasted through life, and led him to seek the utilisation of chemical results rather than to engage in theoretical research. He gained an exhibition at Owens College and afterwards a Royal Exhibition

at the Royal School of Mines, where he secured the Associateship in Metallurgy.

Instead of following this line, he became first chemist at the sugar refinery of Messrs. Abram Lyle and Sons. From 1890 to 1894 he was manager of the Australasian Sugar Refinery, Melbourne, and acted as honorary adviser to the Victorian Government on beet cultivation and sugar manufacture. Leaving for Queensland, he spent a year on improvements of Messrs. Cran and Tooth's juice mills. During the next ten years, at Millaquin and Yengarie, he was general manager for the Queensland National Bank of their refineries, raw sugar mills, and juice mills and plantations. He was also director and chairman of the Bundaberg distillery for several years and justice of the peace for the territory. In 1906 he inspected tropical and sub-tropical agriculture in the East, but owing to failing health he returned to England.

On the death of Mr. B. E. R. Newlands, his father-in-law, Eastick took over the analytical and consulting practice of Newlands Bros. at No. 2, St. Dunstan's Hill, E.C. He took out a number of patents relating to sugar, and contributed important sections on the theory of filtration and on filtration in sugar factories and refineries to the English edition of Buehler's "Filters and Filter Presses."

Eastick leaves a widow, four daughters, and three sons, the latter of whom are carrying on the traditions of their father in applied chemistry. Tribute will always be paid to his memory by his many pupils, co-workers, and employees, and by all who were acquainted with him for his never-failing kindly advice and aid.

L. J. DE WHALLEY.

ERNEST GEORGE HILL.

BORN FEBRUARY, 1872; DIED JUNE 28TH, 1917.

PROFESSOR ERNEST GEORGE HILL, who died on June 28th, 1917, at the Ramsay Hospital, Naini Tal, from an abscess on the liver, was born in February, 1872, and was educated at Oxford, obtaining the B.A. and B.Sc. degrees of that University.

In 1895 he was appointed to the Indian Educational Service, and took up his duties as Professor of Natural Science at the Muir College, Allahabad, on December 26th of that year. He remained on the staff of the Muir College for the rest of his life. In 1911

he acted as Principal of the College, and was permanently appointed to that post in 1913.

He was for many years a Fellow of the Allahabad University, and was elected Dean of the Faculty of Science.

The Muir College of Allahabad is the most important Government College in the United Provinces, and takes the first place among the Colleges affiliated to the Allahabad University, which controls the college education of the province. The Muir College has always been regarded as a model. The buildings are fine and splendidly situated in beautiful grounds, and teaching work there is not handicapped by the very large classes which make college work so difficult in Calcutta. In these circumstances, and with this environment, Hill took a keen interest in his teaching work and remained throughout his career essentially an educationist.

In order to help his students, he prepared and published tables for qualitative chemical analysis and a handbook of practical chemistry, and his research work in chemistry was undertaken primarily with the object of making the teaching of his subject more real and interesting to his students. About that time Government officials were producing monographs on Indian industries, and Hill's attention was directed to them, with the result that he undertook a number of researches into the constitution of Indian products, and used these to stimulate the interests of his students. As in many other branches of study in India then, the courses of schools and colleges were still too rigidly modelled on European syllabuses, and were apt to be followed by the students as exotic and unpractical studies, necessary for a degree, but of no other value.

Like all those who become seriously interested in University work in India, Hill felt the importance of improving the teaching in schools in order to secure a better foundation for college education, and together with Mrs. Hill he prepared a scientific reader for use in schools.

As Principal of the Muir College and Dean of the Faculty of Science of the University of Allahabad, he was able to exert a very considerable and beneficial influence on education in the province. He was a good disciplinarian, commanding respect from his pupils, whilst at the same time he was on excellent terms with them and with his staff. He was a good cricketer and a keen sportsman; these are very valuable qualifications for anyone responsible for college education in India.

In 1910 and 1911 he rendered valuable services in connexion with the educational section of the Allahabad Exhibition.

Hill's original work in chemistry was directed partly to a study

of Indian products and partly to purely scientific problems of physical chemistry. His interest in the latter is probably to be traced to Oxford, where he returned to work during one of his furloughs. The research work started at this time secured for him the Sc.D. degree of Dublin University. A paper on "The Hydrolysis of Ammonium Salts by Water" (T., 1906, **89**, 1273), and another jointly with Dr. A. P. Sirkar on "The Electrical Conductivity and Density of Solutions of Hydrogen Fluoride" (*Proc. Roy. Soc.*, 1909, [*A*], **83**, 130), indicate the trend of his work in this field.

The first Indian product to attract his attention was the salty and alkaline earth which extends over considerable tracts in Northern India. In 1903 he published a note (P., 1903, **19**, 58) on the analysis of the salts contained in this soil. Afterwards he turned his attention to organic products, and published papers on "The coloured constituents of *Butea frondosa*" (P., 1903, **19**, 133), "A new colouring matter from *Nyctanthes Arbor-tristis*" (T., 1907, **91**, 1501), and "The root bark of *Calotropis gigantea*" (T., 1915, **107**, 1437)—the last two papers being written conjointly with Dr. A. P. Sirkar. The colouring matter from *Nyctanthes Arbor-tristis* was obtained in crystalline condition, assigned the formula $C_{20}H_{26}O_3{\cdot}OH$, and named *nyctanthin*. It was subsequently found by A. G. Perkin in *Cedrela toona* (T., 1912, **101**, 1538). From the milky latex which exudes from the broken roots of *Calatropis gigantea*, Hill and Sirkar succeeded in isolating two crystalline substances, melting at 140° and 210° respectively. These were shown to be the *iso*valerates of two alcoholic substances, *mudarol*, $C_{30}H_{47}O{\cdot}OH$, and *akundarol*, $C_{38}H_{61}O{\cdot}OH$. These alcohols were shown to give colour reactions very similar to those of cholesterol and phytosterol; on oxidation, they gave mudaric and akundaric acids respectively. In addition to these, the latex was also found to contain an oily substance, a hard, resinous substance, and a trace of alkaloid.

In addition to his work as chemist and educationist, Hill was for some time Meteorological Reporter to the Government. He also took a considerable part in the general life of the City of Allahabad. He was an enthusiastic cricketer and rider in paper-chases, and was very popular with the other Europeans in the station. For some time he was a member of the Municipal Board, where his presence was welcomed by the educated Indians, who appreciated his business capacities.

E. R. Watson.

GEORGE THOMAS HOLLOWAY.

BORN OCTOBER 19TH, 1863; DIED OCTOBER 24TH, 1917.

GEORGE THOMAS HOLLOWAY, who died on October 24th, 1917, was born at Battersea on October 19th, 1863, and after being educated privately, entered the Royal College of Science and School of Mines, London, in 1881. Here he devoted special attention to chemistry, and obtained the Associateship of the Royal College of Science in 1884. He then served for two years as assistant demonstrator, originally under Sir Edward Frankland, and later under Sir T. E. Thorpe. He was elected a Fellow of the Chemical Society on March 4th, 1886. He afterwards proceeded to Newfoundland, and studied the resources of that colony, and also of the east of Canada. Returning to London, he commenced practice in Chancery Lane, in 1888, as analyst, assayer, and consulting metallurgist. The following year he opened testing works at Limehouse for the examination of ores on a commercial scale. In 1910 his offices and laboratories were removed to 13 Emmett Street, Limehouse. He specialised in the treatment of tin ores and the rarer metals associated therewith. He was consulted by Government departments and many mining companies. Among other work, reference may be made to inquiries, conducted for the Transvaal Chamber of Mines, in connexion with osmiridium occurring in banket ore, and the development of a zinc smelting industry in South Africa. In 1915 he was appointed Chairman of the Royal Ontario Nickel Commission, and to this work the remainder of his life was chiefly devoted. Despite an enfeebled frame and the dangers from submarines, he twice visited Canada in connexion with this inquiry; he also visited Scandinavia, and interviewed, or corresponded with, all the chief makers and users of nickel in the United Kingdom. The report, which was issued shortly before Mr. Holloway's death, occupies more than 800 pages, and is the most complete and trustworthy document which has appeared in reference to the supplies, extraction, and uses of nickel. As a result of this report, a large nickel refining plant has been established on Lake Erie, at Port Colborne in Ontario. This refinery will deal with Sudbury and other nickel–copper mattes which were formerly refined at New Jersey., U.S.A. Mr. Holloway was for years a frequent attendant at the meetings of the Chemical Society, and was interested in the Institute of Chemistry, for which body he acted as examiner in metallurgy. He was an enthusiastic supporter of the Institute of Metals; but perhaps his fullest sympathy was with the Institution of Mining and Metallurgy, on the council

of which he served for many years, and filled the office of vice-president. He was a member of the London section of the Society of Chemical Industry, and a not unfrequent contributor to the journal of that society. Among other appointments, he had served as examiner in metallurgy in the University of Birmingham, assistant examiner to the Board of Education, and juror in the Franco-British Exhibition of 1900. His clearness of intellect, kindliness of manner, unassuming character, and perfect honesty of disposition endeared him to a wide circle of friends, not only in this country, but throughout the British Empire. He was an honorary member of the Chemical, Metallurgical, and Mining Society of South Africa, and acted as corresponding member for the United Kingdom. With a few words taken from the Journal of the South African Society this short notice may suitably close: "It may be fittingly said of him that men of his high character and conduct do much to raise the status of the profession of which he was so distinguished a representative." T. T.

EDMUND ALBERT LETTS.

BORN AUGUST 27TH, 1852; DIED FEBRUARY 19TH, 1918.

EDMUND ALBERT LETTS was born at Sydenham, Kent. His father, in addition to Clare Lodge in Sydenham, owned South View in the Isle of Wight, and there Letts appears to have spent the happiest part of his boyhood, for in later years he often spoke of the place with affection.

His education began at Bishop Stortford School, and was continued at King's College, London, after which he studied at the Universities of Vienna and Berlin.

In 1872 he became chief assistant to Crum Brown in the Chemical Department of Edinburgh University. Four years later, at the early age of twenty-four, he was appointed first professor of chemistry in University College, Bristol, a post in which he was followed by Ramsay. In 1879 he was elected to succeed Andrews in the chair of chemistry in Queen's College, Belfast, and this position (subsequently changed to a professorship in the Queen's University of Belfast) he held until 1917. After his retirement, he spent part of his time in the south of England, and in January, 1918, he left Belfast on a visit to Ventnor. He was a keen cyclist, and took his bicycle with him, spending his time riding about the neighbourhood in which he was staying. On the evening of

February 18th he was out by moonlight, and, while coming down Zig-zag Road about 7.30 p.m., he lost control of his machine and crashed into a wall. He never fully recovered consciousness, and died the following morning about 10 a.m.

His scientific work falls into three main divisions. Up to 1890, his main interest lay among the organic compounds of phosphorus and sulphur, and his investigations in this field gained him the Keith Prize, which was awarded to him in the period 1887—1889 by the Royal Society of Edinburgh. Thereafter he carried out researches on atmospheric carbon dioxide until 1902. His final work was concentrated on the sewage problem, and the results are to be found in Appendix VI. of the 5th Report of the Royal Commission on Sewage Disposal, and also in Appendix III. to the 7th Report of the same body, the work being done in conjunction with Dr. Adeney and Mr. E. H. Richards.

To speak of Letts's personal side is a difficult task for one who only knew him towards the end of his life; but one characteristic stands out above all others—his unfailing kindness to a new and younger colleague. He had complete trust in his staff and showed an unfeigned pleasure in the research output of the laboratory, whether it was his own or was carried out by others, for he had not a spark of that jealousy which at times induces a senior to appropriate the work of a junior colleague. In the distribution of research students among the members of the staff he was more than generous, and his colleagues never had to fear that a student trained by them would be appropriated by Letts as soon as merit was shown. This was not due to indifference, for in his own research room he carried on a steady stream of investigations.

In his personal characteristics, Letts was one of that rare species, "a fine old English gentleman." His reserve, his innate dignity, his impressive presence, and his command of polished oratory all stood him in good stead in the lecture theatre of a university where the students are noted for their high spirits; and the same qualities were valuable to him in other academic relations, for he was one of the leading figures on the staff.

As a chemist, he had a tenacity of purpose so strong that once he had begun an investigation he would never leave it until he was sure that he had carried it as far as he could. "So-and-so used to tell me to drop it," he sometimes said, "but I always find that something comes out if one holds on long enough." He was a neat manipulator and an expert glass-blower.

His outlook on chemistry was a wide one, and his interests tended towards what he called "the philosophy of chemistry." His book, "Some Fundamental Problems of Chemistry, Old and New,"

showed that he was alive to the most recent developments of the subject, and, by its originality in the choice of subjects, it stands apart from the ordinary run of text-books.

He was a Fellow of the Royal Society of Edinburgh and of the Institute of Chemistry. In 1881, the Royal University of Ireland conferred on him, *honoris causa*, the degree of D.Sc., and in 1909, when the Queen's University of Belfast was founded, he was one of the first members of Senate appointed. A. W. S.

PETER MacEWAN.

BORN MAY 29TH, 1856; DIED MAY 16TH, 1917.

PETER MACEWAN, of Highgate, London, who was elected a Fellow of the Chemical Society in 1886, was born at Lochee, Forfarshire, on May 29th, 1856. He was educated locally, and was apprenticed to pharmacy with Mr. John Peebles (now Judge Peebles, of Kirkcaldy), and afterwards became an assistant in his uncle's business at Dundee. His instruction in chemistry was obtained under Mr. Frank Young at the Dundee Science Schools, now the Technical College. He passed the qualifying examination of the Pharmaceutical Society in 1878 and became a pharmaceutical chemist in 1880, acting for a short time as a pharmaceutical tutor. An analytical chart for chemistry students which he devised received a wide recognition for utility. In 1882 he was appointed Secretary in Scotland of the Pharmaceutical Society, took charge of the North British branch in Edinburgh, and made all arrangements for the removal to the present premises. A good deal of his time was spent in chemical research work during his tenure of office, one of the first pieces of work being on the iodo-allyl compounds. He was led to take this up by receiving a sample of liniment of iodine which had caused severe blistering when applied to the skin. An investigation showed that the liniment had been compounded with methylated spirit, and he found that allyl alcohol present in the wood spirit used for denaturing purposes had formed an iodo-allyl compound of a particularly irritating nature. Referring to this research, he was fond of recalling how, his eyes streaming with tears, he received visitors to the Pharmaceutical Society's Museum, and it was sometimes assumed that he was suffering from great grief instead of from his devotion to science. The unstable character of sweet spirit of nitre and the changes that take place on keeping attracted his attention. He found that the diuretic

properties of this old galenical were not due entirely to ethyl nitrite, because old specimens from which ethyl nitrite had disappeared still retained considerable medicinal activity. He simplified the process of estimating the strength of the spirit, and when the late A. H. Allen, of Sheffield, devised the nitrometer, it became possible for the pharmacist to estimate the strength of sweet spirit of nitre within five minutes. Mr. MacEwan also directed attention to the large proportion of sodium carbonate, from 20 to 35 per cent., present in some samples of sodium nitrite, and showed that there should be no difficulty in obtaining a product containing 98 per cent. of sodium nitrite if lead or copper were employed as deoxidising agents for the nitrate. Several of his papers dealt with essential oils, particularly camphor oil and eucalyptus oil, these being at that time recent introductions into medicine. In after years, Mr. MacEwan often regretted that his work on camphor oil was not completed, but he had succeeded by distillation in separating out several of the constituents of this complex substance. The chemistry of Calabar bean and the preparation of solution of bismuth ammonio-citrate were other investigations which he undertook, and he substantially enhanced the interest and value of the scientific meetings of the North British branch of the Pharmaceutical Society. The allocation of a portion of the Hanbury collection of Chinese drugs to the museum caused Mr. MacEwan to take up the study of Chinese, and he obtained sufficient acquaintance with that difficult language to enable him to make translations of the labels and classify the drugs intelligently. In 1885 he was appointed assistant editor of *The Chemist and Druggist*, having attracted the attention of the editor by a clever and laborious codification of the chief pharmacopœias of the world, which he carried out with the object of forming a basis for an international pharmacopœia. On the retirement of Mr. A. C. Wootton in 1899, he succeeded to the editorship, and from that time specialised in the various legal enactments dealing with the drug trade, for example, the Medicine Stamp Acts, the poisons laws, the Sale of Food and Drugs Acts, and the spirit laws, while keeping always in close touch with the latest developments in chemical and pharmaceutical science. He contributed a number of papers on ethical subjects to various pharmaceutical bodies. He visited America in 1893, and made many friends among American men of science. In 1909 he went to Germany for the International Congress of Pharmacy, where, in collaboration with Mr. G. P. Forrester, F.C.S. (who has been interned in Germany since the outbreak of war), he contributed a paper on the standardisation of potent medicinal preparations. He

was a member of the Society of Chemical Industry, a corresponding member of the Société de Pharmacie, Paris, Secretary of the Commission on Variation in Activity of Potent Drugs (set up by the International Congress of Applied Chemistry in 1909), and connected with most of the drug trade organisations of this country. Mr. MacEwan was the author of "The Art of Dispensing," which is the standard work in the English language on the dispensing of medicines, and of "Pharmaceutical Formulas," a receipt book for chemists and druggists, of which works many thousand copies have been sold. Of his personal character much could be written, but the outstanding features were his kindness, geniality, "pawky" humour, and indefatigable industry. The strong love of his native country which he had was shown by his yearly visits to the Highlands and his connexion with such bodies as the Scottish Corporation, the Caledonian Society, and the London Forfarshire Association. His end came with great suddenness from an attack of apoplexy, although during the previous winter he had had a severe illness, which acted as a warning. Thus he "laid down the well-worn tools without a sigh" in the plenitude of his powers and with his faculties unimpaired, bequeathing to his friends a lofty ideal and an inspiring example. S. W. W.

LUDWIG MOND.

BORN MARCH 7TH, 1839; DIED DECEMBER 11TH, 1909.

LUDWIG MOND was born at Cassel on March 7th, 1839. His father, Moritz B. Mond, was a merchant of that city. His mother's maiden name was Henriette Levinsohn.

Mond was educated at the Realschule and the Polytechnic School at Cassel, and then went, in 1855, to study chemistry under Hermann Kolbe at Marburg.

In the following year, 1856, he proceeded to Heidelberg, and so, having followed the great teacher through two institutions, still marked by his influence, he came under the actual control of Robert Wilhelm Bunsen. From him, during a three years' course, Mond undoubtedly acquired that absorbing love of pure chemical science that was so characteristic of him in after life.

His introduction to industrial activity took place at a small Leblanc soda works at Ringenkuhl, near Cassel. Here, the continual waste of sulphur speedily attracted his attention, and he began in 1860 those researches which ultimately led to the invention of his well-known recovery processes.

He left Ringenkuhl to become manager of a factory at Mainz for producing acetic acid by the distillation of wood, and from there went to Cologne to engage in the manufacture of ammonia from waste organic matter, especially leather.

After spending some time in one or two other factories, both in Germany and Holland, he came to England in September, 1862.

Mond's experience at Ringenkuhl led to his patenting a process for the recovery of sulphur from Leblanc alkali waste by atmospheric oxidation, lixiviation, and subsequent separation of sulphur by treatment of the liquors with hydrochloric acid. This process was patented in France in December, 1861, and in England in August, 1862.

Entering the works of John Hutchinson and Co. at Widnes in order to demonstrate the working of his process, and if possible to sell his patent, Mond speedily found that it was not entirely adapted for large-scale operations, where the cost of labour was an important consideration, and he patented an improvement on September 8th, 1863.* This consisted of carrying out the oxidation in the "black-ash" lixiviating vats by blowing air through the waste and repeating the operation after one or two washings with water. Subsequently, Mond introduced the use of waste liquor from chlorine stills in place of fresh hydrochloric acid for the decomposition of the soluble sulphur compounds, with the separation of free sulphur.

In 1864 he undertook the construction and management of a Leblanc soda works at Utrecht, and remained there for three years.

Shortly before his return to Widnes, in 1867, he married his cousin, Frida Löwenthal, daughter of Adolf Löwenthal, who was one of the pioneers of German electro-plating and electro-chemical industry. Lifelong familiarity with scientific problems eminently fitted Mrs. Mond to be the companion of such a man as her husband, and to the end of his life she never failed to take the most intense interest in all his work.

When Mond returned to England, and became a naturalised

* "On the manufacture of sulphur from alkali waste in Great Britain," by Ludwig Mond:—Read before the British Association at Norwich, 1868. *Chem. News*, October 2nd, 1868:—

"On the recovery of sulphur from alkali waste," by Ludwig Mond; Pamphlet published by W. B. Jones & Co., South Castle Street, Liverpool.

"On the probable effect of the general adoption in Great Britain of Mond's process for the Recovery of Sulphur from Alkali waste from a mercantile point of view," being a paper communicated to the River Pollution Commissioners at their request by Ludwig Mond—G. G. Walmsley, 50, Lord Street, Liverpool, 1870.

British subject, he rejoined Messrs. Hutchinson, perfected his sulphur recovery in their works, and introduced it to many others. This and the Schaffner process continued to be worked until they were displaced by the Chance process.*

In 1872 Mond made the acquaintance of Ernest Solvay, a Belgian chemist, who was interested in the process of making carbonate of soda invented by Harrison Gray Dyar and John Hemming in 1838.† Solvay, in association with his brother Alfred, had built and was running a small factory at Couillet, near to Charleroi. They were not by any means the first who had endeavoured to convert the simple reaction of Dyar and Hemming into a manufacturing process, nor was their experience of difficulties dissimilar from that of their predecessors either on the technical or the financial side; but, by the application of scientific skill, the exercise of boundless patience and tireless application to work, they were beginning to surmount one obstacle after another.

While at Messrs. Hutchinsons' works at Widnes in 1862, Mond had become the friend of Mr. (now the Rt. Hon. Sir) John Tomlinson Brunner, who was in the commercial department of that firm, and when a study of Solvay's works convinced Mond that there were chances of a brilliant future for an ammonia-soda process, he entered into partnership with Brunner and obtained a licence to work Solvay's process in England.‡

With some difficulty they obtained sufficient capital to enable them, in 1872, to purchase the Winnington Park Estate, Northwich, from Lord Stanley of Alderley, and to erect small works thereon. Whereas the Leblanc process starts with solid salt, the ammonia-soda process requires salt in solution, and so a Cheshire site was selected for the works, because saturated brine was readily obtainable in the immediate neighbourhood.

With the starting of the works in 1873 there commenced a period of trouble that lasted for six or seven years. Although the reactions $NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl$ and $2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$ take place most readily as discovered by Dyar and Hemming, the process becomes more complicated when the raw materials are impure, when all operations have to be carried out in closed vessels to avoid loss of ammonia, and when the apparatus itself is apt to be destroyed by the corrosive action of some of the reagents. The problem of convert-

* G. Lunge, "Sulphuric Acid and Alkali," 2nd edit., 2, 827–851.

† Dyar and Hemming, E.P., 7713 of 1838: Improvements in the manufacture of carbonate of soda.

‡ E.P., 3131 of 1863, E. Solvay—Apparatus by means of which the formation of carbonate of soda by direct combination is rendered practically available for manufacturing purposes.

ing an interesting chemical experiment into a lucrative commercial process had baffled all the earlier manufacturers, and although Solvay had achieved quite an appreciable measure of success, the gigantic task of evolving an economical continuous process carried on in scientifically designed apparatus was reserved for Mond.

No man was better fitted for the undertaking. Endowed with a quick and fertile brain, he readily grasped the reasons why troubles arose, and his thorough training in pure science enabled him to guard against their recurrence. A tireless worker himself, he had no patience with those whose energies were not sustained. Although his house was within one hundred yards of the works, he frequently spent his nights in the factory, taking such rest as he could secure on a bed arranged in the foreman's office in the midst of the plant. Gifted with powerful determination, he could never contemplate his own failure, and had little sympathy for such as admitted theirs.

A friend was once asking him not to be too hard on a man who had failed to achieve a successful result in a task which had been allotted to him, and urged that the man had done his best, when Mond said: "Heaven help the man who does his best and fails; there is no other hope, and I have no use for him."

By living in the midst of his work, in those early days, Mond set a wonderful example to his assistants and men. His methods of manufacture were absolutely scientific; there was no "rule of thumb" practice. Appearance, taste, and smell did not satisfy him; he took nothing for granted.

One characteristic example is perhaps worth quoting, because it is so typical of his method of teaching in a manner not easily forgotten. Three of his assistants once reported to him that a certain boiler employed for heating brine was constantly getting stopped up with sand. Mond expressed surprise, and accompanied the three to view it. He was shown the sand, and listened for a short time to the various theories propounded of how it came from the brine shaft. He suddenly turned to one and said: "Bring me some hydrochloric acid." When provided with this, he poured it over the "sand," and this promptly dissolved with free evolution of carbon dioxide. Turning to the assistants, he said: "Now where is your sand? You are a nice lot of chemists."

For seven arduous years Mond struggled with the problems which the process presented; but gradually, by successive inventions, he so transformed the methods of manufacture that by the year 1880 he was able to claim that the ammonia-soda process was a commercial success.

Brunner, Mond and Company were not without competitors in

working the Solvay process in England, for, in 1874, Messrs. Richards, Kearne, and Gascoigne had started works at Sandbach in Cheshire, under licence from Solvay. Their venture, however, was not successful, and the works were sold to Brunner, Mond and Company in 1878.

In 1881 the undertaking was converted into a limited company with £600,000 capital, and works at Winnington and Sandbach. Brunner and Mond became managing directors. To-day the nominal capital stands at £10,000,000, and the company owns six factories and has controlling or other interests in several more.

In his endeavour to produce soda more economically by the ammonia process than it could be manufactured by that of Leblanc, Mond was naturally anxious to obtain cheap ammonia. We have seen that, in 1861, he was engaged in the production of ammonia from waste material of animal origin, and he stated that he then observed that the yield by no means corresponded with the nitrogen in the raw material.

In 1879 he determined to make a complete study of the problem of how to manufacture ammonia cheaply.* With the object of testing the value of already known processes for obtaining ammonia from the nitrogen of the air, he engaged Mr. Joseph Hawliczek to carry out the experimental work. All the processes investigated gave unsatisfactory results, with the exception of one, and that was the barium cyanide process invented by Margueritte and Sourdeval. This consists in heating a mixture of barium carbonate with carbon in the presence of nitrogen, and then treating the resulting barium cyanide with steam, thus producing ammonia and regenerating the barium carbonate.

The experiments proved so promising that Mond designed apparatus for carrying out the manufacture on a fairly large scale. The formation of cyanides by this method, however, requires a temperature of from 1200° to 1400°, and Mond ultimately found that his special clay retorts would not last in this great heat, and he was compelled reluctantly to abandon the process. Among the tested processes for obtaining ammonia from the nitrogen of the air was one patented by Rickman and Thompson, who claimed that by passing air and steam through a deep coal fire the nitrogen is to a certain extent converted into ammonia. Mond found that it certainly yielded a considerable quantity of ammonia, but he discovered that, if the same coal were burned in an externally heated tube in a current of steam alone, it gave double the amount. He made large scale experiments in this direction, but came to the

* Presidential Address to the Society of Chemical Industry, 1889, by Ludwig Mond.

conclusion that, although the yield of ammonia was large, the process could never be economical. He saw, however, that if coal could be burned in gas producers by a mixture of air and steam, the plant could be simple, and the gas obtained could be utilised in the same way as ordinary producer gas.

He therefore constructed gas producers and ammonia-absorbing plant at Winnington, and experimented with different classes of fuels for a number of years. These showed that the yield of ammonia varied inversely with the temperature at which the producer was worked, and that the temperature could be controlled by regulating the amount of steam admitted with the blast; the lower the temperature, the higher was the yield of ammonia. Considering the cost of steam, he found that the best practical results were obtained by introducing about two tons of steam for every ton of fuel gasified. He succeeded in converting one-half of the nitrogen existing in the fuel into ammonia, getting about 8 kilos. of ammonia per ton gasified. The gas obtained (now known as "Mond gas") contained about 15 per cent. of carbon dioxide, 10 per cent. of carbon monoxide, 23 per cent. of hydrogen, 3 per cent. of ethylene, and 49 per cent. of nitrogen. This was used for heating furnaces and working gas engines, and proved so satisfactory that a large plant was installed at Winnington.

Having now satisfied himself that his process could yield a cheap gas suitable for almost every manufacturing operation, Mond sought to extend its use throughout the world. He formed the Power Gas Corporation to grant licences under his patents, to act as technical advisers to, and erect plants for such manufacturers as desired to employ the gas.

Mond's statement that his gas could be generally employed in manufacture met with strong criticism from iron makers, who said that, on account of its low calorific power, it could never be used for making steel.

With characteristic energy, Mond immediately built a Siemens steel furnace at Winnington and made steel there for some weeks, inviting the steel makers to come and see it.

Recognising that the gas was eminently suitable for small furnace and foundry work, and that it ensured smokeless combustion, Mond was instrumental in founding the South Stafford Mond Gas Company in the heart of the Black Country, at Tipton, near Dudley Port. Here, fuel is gasified in Mond producers, and, after purification, the gas is compressed and delivered into mains that convey it to consumers in about 160 works.

Mond stated in his Presidential Address to the Society of Chemical Industry in 1889 that if one-tenth of the 150 millions

of tons of fuel annually consumed in England were treated by his process, the production of sulphate of ammonia would be large enough to enable us to supply the whole of the Old World, and would render us independent of the New for supplies of nitrate of soda for fertilising purposes. He spoke, of course, in ignorance of the enormous consumption of nitrates which a modern war would involve, but when we, with our later knowledge, recognise the readiness with which an "Ostwald" process can convert ammonia into nitric acid, we can confidently depend upon a moderate development of his process rendering England independent of Chile.

English Mond gas producer works in operation are using bituminous coal, but the Italian installations at Lucca and Orentano are working with lignite. The process has also been applied to the gasification of peat.

In his anxiety to obtain cheap ammonia for the ammonia-soda process, Mond's attention was attracted to by-product coke ovens, and, as the soda process requires coke for its limestone burning, Brunner, Mond and Company erected the first English installation of Semet-Solvay ovens.

In 1884, Mond made London his regular place of residence in order to live in close association with scientific societies. He first resided in Park Crescent, but later acquired The Poplars, 20, Avenue Road, Regent's Park. This house formed his headquarters all the rest of his life; there he started a laboratory for his research work, and made his house a centre for scientific and artistic friends. In order to escape the rigours of the English climate, he spent most of his winters in Rome, at his house the Palazzo Zuccari.

One of the first inventions emanating from the new laboratory was a gas battery (*Proc. Roy. Soc.*, 1888, **46**, 296). Mond obtained the assistance of Dr. Carl Langer, and attempted to discover whether it was possible for a gas so rich in hydrogen as Mond gas to be as directly converted into electricity as pure hydrogen. Starting with the construction of the cell described by Lord Justice Grove in 1839, and working with pure hydrogen, they found that its operation was so tardy that they were led to seek for more suitable electrodes.

After a long series of experiments, they evolved a cell which consisted of a number of elements. The strips of platinum foil as used by Grove, partly immersed in dilute sulphuric acid, gave place to porous diaphragms of inert material, such as plaster of Paris, impregnated with acid, and these were covered on each side with very fine platinum leaf perforated with numerous small holes and covered with a thin film of platinum black. It became

practically a dry battery. A number of these elements are placed side by side with non-conducting frames between to form chambers, so that hydrogen can be passed along one side of the element while the other side is exposed to air.

Mond and Langer found that a battery consisting of seven elements, with a total effective surface of half a square metre, contained 2·5 grams of platinum leaf and 7 grams of platinum black, and gave a current of 2 amperes and 5 volts or 10 watts, equal to nearly 50 per cent. of the total energy obtainable from the hydrogen absorbed. Having so constructed an efficient battery, they next proceeded to employ producer gas in lieu of hydrogen alone. They discovered that unless the gas were deprived of its carbon monoxide and hydrocarbons prior to use, the efficiency of the platinum black rapidly disappeared. In seeking for a cheap method of removing these gases at the temperature of gases leaving the producer, they discovered that if such gases were passed with the steam which they contained over finely divided metallic nickel or cobalt, the carbon monoxide was converted into carbon dioxide and carbon, whilst the hydrocarbons yielded carbon and hydrogen.* They found that when the producer gas was thus purified and enriched in hydrogen it yielded good results with the battery; but, unfortunately, the life of the battery itself proved of short duration.

In connexion with the work on the gas battery, Mond undertook a research in company with Sir William Ramsay and Dr. John Shields on the occlusion of oxygen and hydrogen by platinum and palladium (*Proc. Roy. Soc.*, 1894, **58**; *Phil. Trans.*, 1897, **190**; 1898, **191**).

Pressure of other important work unfortunately prevented Mond from solving the problem of how to construct a battery to endow it with a long life.

By 1886 the ammonia-soda process had developed to such an extent that it had become a serious competitor of the Leblanc process; but as such it possessed one defect, inasmuch as it wasted all the chlorine of the sodium chloride, and so produced no bleaching powder.

This was recognised by Mond as early as 1882, and he patented a process for manufacturing calcium peroxide to be used as a substitute for bleaching powder. He followed this in 1883 by a process for obtaining hydrochloric acid. In the ammonia-soda reaction, the chlorine remains in solution, in combination with ammonia, along with residual sodium chloride. Mond concentrated this liquor by heat, and, after the removal of the first

* L. Mond and C. Langer, "Improvements in obtaining hydrogen," E.P., 12608 of 1888.

crystals of common salt, obtained the ammonium chloride in a solid form. This, on treatment with sulphuric acid, yielded hydrochloric acid and ammonium sulphate.

In 1886 (E.P., 66 of 1886) he invented a process for obtaining chlorine by passing the vapour of ammonium chloride over nickel or a similar active oxide to form the corresponding chloride with liberation of ammonia, subsequently treating the chloride with hot dry air to liberate chlorine and regenerate the oxide. By employing superheated steam in place of dry air, he obtained hydrochloric acid instead of chlorine (E.P., 65 of 1886). The process for the manufacture of chlorine was installed at Winnington, and bleaching powder was made by it for several years. The concentration process for obtaining ammonium chloride was superseded by a cold one, wherein the liquors were reduced in temperature by freezing machines until the ammonium salt separated. This was found to yield a product of great purity, an essential property for a salt which had to be volatilised. The dried ammonium chloride was volatilised by heat, and the vapours were passed over nickel oxide. This yielded nickel chloride and allowed free ammonia to pass forward for absorption in water and eventual return to the soda process. Chlorine was obtained by passing a current of hot dry air over the nickel chloride, and was utilised in Deacon chambers for the production of bleaching powder. In order to secure the exposure of a large surface to the action of the gases, Mond made up the nickel oxide into pills by mixing it with china clay and pressing it between rollers with hemispherical cavities. He found that when these pills had been in use for some weeks they became black, swelled up, and ultimately fell into powder. Investigation showed that, in this condition, they contained a considerable quantity of carbon. This was found to owe its origin to the constituents of the so-called "inert gas" which was employed to sweep out the last trace of ammonia from the apparatus before proceeding to evolve chlorine. This gas was obtained from the exits of the ammonia-soda precipitation towers, and consisted of nitrogen mixed with some carbon dioxide and carbon monoxide. A study of the behaviour of these gases in the presence of nickel oxide and their action on metallic nickel led Mond and Langer not only to devise the method previously mentioned of removing carbon monoxide from producer gas, but also to the discovery of nickel carbonyl.*

The plant employed for the volatilisation of ammonium chloride had to be of special construction on account of the violent attack of the vapour on most metals. The valves which were required

* "The history of my process of nickel extraction," by L. Mond, *J. Soc. Chem. Ind.*, 1895, **14**, 945.

for effecting the changes of current were made of nickel. Although laboratory experience had shown this metal to be proof against attack by ammonium chloride vapour, the valves in the manufacturing process soon became leaky, and were found to be coated with carbon. Mond and Langer were thus led to make a careful study of the action of carbon monoxide on nickel with the view of ascertaining whether a definite compound of nickel and carbon was formed. In the course of experiments, finely divided nickel was treated with pure carbon monoxide in a glass tube at varying temperatures for a number of days, and was then cooled in a current of carbon monoxide before it was removed from the tube. In order to keep the poisonous carbon monoxide out of the atmosphere of the laboratory, the gas escaping from the apparatus was connected to a Bunsen burner and lighted. To their surprise they found that, while the tube was cooling, the flame became luminous and the luminosity increased as the temperature fell below 100°. The flame gave a mirror on a cold porcelain plate, and when the glass exit tube of the apparatus was heated, a metallic mirror was obtained inside, whilst the Bunsen flame lost its luminosity. The mirror was found to consist of pure nickel. Eventually they were successful in discovering that, at a temperature below 100°, nickel combines with carbon monoxide to form a tetracarbonyl which is a colourless liquid boiling at 43° and solidifying at 25° to form needle-shaped crystals (Mond, Langer, and Quincke, T., 1890, **57**, 749; Mond and Langer, *ibid.*, 1891, **59**, 1090).

Owing to the disintegration of the nickel pills, Mond substituted magnesia and obtained satisfactory results. The chlorine process was carried on for several years; but the plant proved costly in repairs, and the heat losses were considerable. Although the raw material, ammonium chloride, was ready to hand in solution with other compounds, the separation and drying of the pure salt could not be effected cheaply, and proved a serious handicap to a process which had to compete with those that started with common salt. The process was therefore abandoned in favour of one patented by Carl Hoepfner, by which zinc oxide and calcium chloride under treatment with carbon dioxide yield zinc chloride and calcium carbonate. The zinc chloride on electrolysis gives chlorine and pure zinc. Thus the residual liquors from the ammonia-soda process were made to yield their chlorine, and the zinc was obtained in a state that commanded a high price.

In investigating the properties of nickel carbonyl, Mond was impressed with the ease with which nickel could be converted into a volatile gas by the action of carbon monoxide, and recognised that it might afford a method of separating this metal from others on a manufacturing scale. He was at first averse to undertaking

the creation of an entirely new industry himself so late in life, and proposed to sell his patent; but, as he failed to find a purchaser, he erected plant in 1892 in the Wiggin Nickel Works at Smethwick, near Birmingham, and placed it in the charge of Dr. Carl Langer. For such a novel process, all the plant had to be designed and constantly altered through the first four years of arduous work. When the practicability of the process had been fully demonstrated, Mond formed the Mond Nickel Company, and handed over to it the future developments of the manufacture. He became its first chairman, and retained the office until his death. In addition to the labour involved by the construction of large works at Clydach, near Swansea, the company had to acquire and develop mines and ore-handling plant in Ontario, Canada. Although in all this work he was ably assisted by his two sons, together with Dr. Langer and Dr. B. Mohr, the bulk of the work fell upon Mond, for, with his characteristic thoroughness, he insisted upon personally examining every detail.

He had the satisfaction of seeing his process become of immense commercial importance, and the company rewarded with phenomenal success. The Clydach Works, managed by Dr. Langer, have been repeatedly enlarged, and now produce annually upwards of 3000 tons of 99·9 per cent. nickel.

The details of the process were well described by Roberts-Austen before the Institute of Civil Engineers in 1898 (*Proc. Inst. Civil Eng.*, 1898, 135). The discovery of such an astonishing compound as nickel carbonyl led Mond to investigate the action of carbon monoxide on other metals. He soon succeeded in preparing iron carbonyl, but found that, at the ordinary pressure, no results were obtained with any of the large number of metals which he employed. At high temperature and under extreme pressure, however, he succeeded later in obtaining carbonyl of cobalt at 100 atmospheres and 200°, of molybdenum at 250 atmospheres and 200°, and of ruthenium at 450 atmospheres and 300° (*Seventh Inter. Congress App. Chem.*, 1909).

The account of this work, carried out with the assistance of Dr. Hirtz and Mr. Cowap, formed the substance of the last publication under Mond's name (T., 1910, **97**, 798).

The four strenuous years devoted to the placing of the nickel process upon a firm industrial basis undoubtedly overtaxed Mond's strength. He had suffered from a weak heart for several years. The unfortunate death of three workmen, due to inhaling some of the poisonous nickel carbonyl, deeply affected him, and the sudden death in Egypt of his daughter-in-law, Mrs. Robert Mond, completely broke him down.

He presided over the Inorganic Section of the Seventh Inter-

national Congress of Applied Chemistry held in London in the summer of 1909, and entertained the members at a garden party at The Poplars, Avenue Road. In the late autumn he suffered much from sleeplessness, and his health visibly declined. He had intended to winter in Rome, but was never sufficiently well to bear the journey. He died at his house on December 11th in his seventy-first year, and was laid to rest on the 14th in the mausoleum at Finchley, which he had built to receive the bodies of himself and his family. The funeral was most impressive. Standing on the top of the wide stone steps which lead to the upper part of the mausoleum, the Jewish Rabbi conducted the service in Hebrew. Ranged below him stood men eminent in science, art, and industry; Mond's two sons, his old partner and friend Sir John Brunner, Ernest Solvay, directors, managers, foremen, and old workmen from the factories with which he was connected, and chemical manufacturers. These, from far and near, along with a group of chemists containing those who had been associated with him in his researches, seemed to represent every phase of his life. Whatever was the sense of personal loss, each felt that science and industry had lost a great man. He was recognised by all as an ideal industrial pioneer. With all his love of pure science, he was never led to make interesting researches which had no definite object. He never undertook work which was unlikely to prove of industrial utility. His financial success was great, but this was not regarded by him as the reward which he desired for his work. He never worked for the purpose of making money, but for the sole object of cheapening manufactured products. In his fortuitous partnership he owed his financial success just as much to the commercial genius of Sir John Brunner as the latter, in turn, was indebted to the scientific ability of Mond.

No words can more fitly describe Mond's attitude of mind in connexion with his work than those used by himself in concluding his presidential address to the Society of Chemical Industry in 1889. He said:

"The statement is frequently made that 'Necessity is the mother of Invention.' If this has been the case in the past, I think it is no longer so in our days, since science has made us acquainted with the correlation of forces, teaching us what amount of energy we utilise, and how much we waste in our various methods for attaining certain objects, and indicating to us where and in what direction, and how far, improvement is possible; and since the increase in our knowledge of the properties of matter enables us to form an opinion beforehand as to the substances we have available for obtaining a desired result. We can now foresee, in most cases, in what direction progress in technology will move, and, in con-

sequence, the inventor is now frequently in advance of the wants of his time. He may even create new wants, to my mind a distinct step in the development of human culture. It can then no longer be stated that 'Necessity is the mother of Invention'; but I think it may truly be said that the *steady methodical investigation of natural phenomena is the father of industrial progress.*"

He had no great faith in the value of teaching technological or industrial chemistry in special laboratories or institutions, for he held that a man could only become a successful industrial chemist when he had received a complete training in pure science.

In his speech to the students assembled at the opening of the Schorlemmer Laboratory for Organic Chemistry, Manchester, in May, 1895, he advised them to devote their attention to the study of pure science alone without giving any thought to immediate practical results.

In order to foster scientific research, Mond purchased a house, formerly the town residence of Lord Albemarle, adjacent to the Royal Institution, and after converting it into a laboratory, fully equipped with apparatus at a cost of £45,000, presented it to the nation along with a sum of £62,000 as endowment, requesting that the building should be called the Davy-Faraday Laboratory. His idea was to provide a place where an investigator could secure the means of pursuing his researches under the best possible conditions without the expenditure of large sums of money.

All through his life Mond never failed to point out to his assistants that, in order to avoid waste of time and for the purpose of securing a favourable start, they should read all that had been published on the subject before they started any new investigation. In his later years, he recognised that in the face of the multiplication of scientific publications it became year by year more difficult to ascertain what had been written. In order therefore to facilitate the consultation of the world's publications, he presented the Royal Society with a sum of £14,000 to defray the cost of the regular compilation of a catalogue of international scientific literature.

Great as was the fortune which Mond amassed, no less princely was his liberality. What he gave privately to those on whom fortune had not smiled is known to very few. It is, however, certain that of those who solicited help from him, none but such as were proved to be unworthy failed to receive it.

Mond was the recipient of the following honours:

He was instrumental in founding the Society of Chemical Industry, and was elected its first president in 1881, and was again president in 1889.

He was elected a Fellow of the Royal Society in 1891.

Doctor of Science (*honoris causa*) of the University of Padua in 1892.

Doctor of Science (*honoris causa*) of the University of Heidelberg in 1896.

Foreign member of the Reale Accademia dei Lincei of Rome in 1899.

Doctor of Science (*honoris causa*) of the University of Manchester in 1904.

LL.D. (*honoris causa*) of the University of Oxford in 1907.

Honorary member of the German Chemical Society in 1908.

Grand Cordon of the Crown of Italy in 1908.

Honorary foreign member of the Royal Society of Naples in 1908.

Foreign member of the Prussian Academy of Science in 1909.

Ludwig Mond was a man with a most impressive presence. He had a large head with a highly developed forehead. Although he was bald on the crown, his hair grew profusely round his neck and always evinced a tendency to curl. His eyebrows were thick and protruded somewhat over his dark, piercing eyes. His beard was full and his features generally were of an Oriental type. His face was capable of expressing extreme gentleness and intense severity. He had a keen appreciation of humour, and in his younger days was almost boyish in his mirth. He possessed a most sociable disposition, formed firm and lasting friendships, and ever preserved a tender regard for those with whom he had associated.

He possessed a sensitive and sympathetic nature, and was ever ready to assist those who were in trouble. He was a keen debater, but very quick in resenting obvious contradiction. The powerful will and firm self-confidence that enabled him to achieve so much made him disinclined readily to weigh other people's opinions against his own. A rapid thinker himself, endowed with a remarkable faculty for mental arithmetic, he was apt to become impatient with those who failed to follow. For him, all information had to be definite and precise; generalities annoyed him. He could not think of a problem unless he had volumes, weights, and temperatures to commence with.

His voice was deep and guttural, and he never so completely lost his German accent as to master the English "w's" and "th's." He possessed the power of obtaining sleep at will, and although an indefatigable brain worker, he could reinvigorate himself by taking half an hour of sleep, terminating almost at the moment he had arranged.

He was a great cigar smoker, and obtained stimulus from the practice. His consumption of a cigar kept pace with the working of his brain. When engaged in the discussion of abstruse problems,

he invariably walked up and down his room smoking, and as he became more and more absorbed in thought, his cigar burned faster and faster.

He was much beloved by his workpeople, who regarded him as an exacting master, but a perfectly just one. He could be, and often was, very angry with any man who was lazy or stupid, but he never kept any bitter feeling towards the delinquent. Much of his anger, too, was assumed for the purpose of making an impression.

During his absence in Rome in 1903, a report reached England that he had died, and obituary notices appeared in some of the newspapers. The news was quickly shown to be false, and on his next visit to Winnington the workpeople met him in torchlight procession, presented an illuminated address of welcome, and made Winnington Park gay with fireworks.

In 1898, to celebrate the twenty-fifth anniversary of the commencement of the works, Sir John Brunner and Dr. Mond presented a handsome building to the company to serve as a pavilion and recreation club for the workpeople. It was built in Winnington Park on the recreation ground. They further entertained their men with their wives and children, to the number of 12,000 individuals, at a *fête* in the park.

His winter residence in Rome developed that great love of the arts which had always been characteristic of him. He was intensely fond of music, and never so happy as when he could offer his hospitality to those who were celebrated in the art.

He was a great admirer of the early Italian painters, and he collected at his London house one of the finest galleries of their works in England. At his death he bequeathed these to the nation.

In an eloquent commemoration of their foreign member, Ludwig Mond, read to the Dei Lincei Royal Academy on April 3rd, 1910, by Raffaele Nasini, the author said:

"He loved Italy with a great love; he loved it on account of its brilliant skies, on account of its beautiful landscapes, the customs of the people, and its ancient art; he loved it in its men of science, in its men of literature, in its men of art. He assisted many provident and charitable institutions in this country; he relieved many disasters great and small, together with his good companion. Italians found in his hospitable house at The Poplars a piece of their own country, where everything spoke of Italy. How many glad remembrances of our country and our countrymen were evoked by Dr. Mond and his amiable family; how much admiration for Italy burst forth from their hearts whilst the Virgin of Tiziano and the beautiful Flora of Palmo il Vecchio were smiling on us.

"Italian science was a great favourite with Mond, and conspicuous grants were received from him by the Chemical Institute of Rome and my Institutes of Padua and Pisa.

"For our grand Cannizzaro he had an intense admiration and profound veneration. He said that his friendship with him was one of the greatest satisfactions of his life. In honour of Cannizzaro he founded in our Academy that conspicuous prize called after him, which will be delivered the first time in 1911, and let it be hoped that it will bear fruit equal to the love entertained for science by him who founded it. Last year (1909) the Italians who met in London for the International Congress of Applied Chemistry wished to show their gratitude to Mond, and on May 30th, in connexion with a splendid garden party given by Mond to the members of the Congress, there was offered to him, on behalf of nearly 500 chemists of our country, a bronze shield, the eminent work of our sculptor, Carlo Fontana, on which Mond's work was symbolised. On presenting it, speeches were made by Professor Ciamician, myself, and Professor Paternò, the latter expressing himself in very appropriate language as follows:

"The prize you have founded and which you wish to adorn with the illustrious name of Stanislas Cannizzaro will be for Italian chemists, now and for ever, a perennial monument of their gratitude towards you. The honour shown to our grand master is an indissoluble link between your name and Italian Science.

Mond in his reply remarked that what he had had in view was to point out to the present and future generations of chemists what splendid results may be obtained from a life of true devotion to science such as had been, and was, that of Cannizzaro."

In addition to the portrait of Mond on the shield mentioned above, there are a marble bust (1896) by Joseph von Kopf, a bronze bust by Henri Glicenstein, a bronze statue (1906) by Ferdinand Seeboeck, a portrait medallion by E. Lanteri (1911), an oil painting by Solomon J. Solomon, R.A., and in Winnington Park stands a lifelike bronze statue by E. Lanteri, unveiled by Sir John Brunner in 1913 amid a remarkable concourse of Mond's old friends. Here, from his granite pedestal, wearing his well-known dust coat and patriarchal soft felt hat, holding a bundle of plans in his hand, the "Old Man" (as he was always called) stands looking at the works he loved so well. To one who sees this effigy daily, the thought often occurs: What would he think of them now? grown even beyond his plans; and a certain amount of satisfaction is derived from the fact that during all this remarkable development the statue apparently stands constantly watching.

Although some years have now elapsed since his death, it is not possible for the country to gauge the value of his work by noting

the size or number of the factories which he was instrumental in creating. The full benefit accruing from it will not be separately assessable from national industrial progress; but for a generation to come England will have reason to remember Ludwig Mond, the great pioneer chemical manufacturer. JOHN I. WATTS.

BENJAMIN HORATIO PAUL.*

BORN 1827; DIED 1917.

BY the death of Benjamin Horatio Paul, in his ninetieth year, there is removed one of the last of the Olympians of the early epical years of British scientific pharmacy. His life pilgrimage, so full of years and honour, was for a long space of its course contemporaneous with the history and progress of the Pharmaceutical Society, to the faithful and fruitful service of which he dedicated so rich a measure of his remarkable talents and energies. The late Dr. Paul was born in 1827, and in his fourteenth year entered the profession of pharmacy at Fakenham. He was one of the group of eight students in the Pharmaceutical Society's original laboratory during the first session of the School of Pharmacy, and in 1845, at the age of eighteen, won the school's first prize in chemistry and the second prize in organic chemistry. While a student in the school he came under the inspiring and formative influence of Pereira, that prince of teachers and master in pharmaceutical science and lore, with whom he formed a life-long friendship, and whose memory he cherished as one of his most precious possessions. Thereafter he studied at Giessen, under Liebig, and in 1848 took the degree of Ph.D. (Giessen). Returning to England, he prosecuted his studies under Graham (the Master of the Mint), acting as one of his assistants, and passed the Major Examination in 1852, the number of his Major certificate being 9. He first contributed to *The Pharmaceutical Journal* in 1846, and in 1856 commenced a notable monthly series of articles on "The Progress of Chemical and Physical Science," which succinctly and with characteristic accuracy summarised and reviewed the advances in these branches of knowledge. He was soon recognised as a leading authority on the pharmaceutical and allied sciences, to the advancement of which his original work then and later materially contributed. In particular, his researches in collaboration with Cownley on the chemistry of cinchona, ipecacuanha, and other alkaloidal drugs, have made permanent additions to the knowledge of these subjects, and his literary labours, which covered a wide scientific range, included contributions to the first edition

* Reprinted, by permission, from *The Pharmaceutical Journal*.

of Watts's "Dictionary of Chemistry," editorship of the English version of the German edition of Payen's "Précis de Chemie Industrielle" (1878), for which he wrote the supplementary chapters on the chemistry of the metals; the editorship for Bohn's series of Bolley's "Manual of Technical Analysis"; the Report, in collaboration with Passmore, of the First International Exhibition at Vienna in 1883; and, in conjunction with Holmes and Passmore, the Report on the Materia Medica Pharmaceutical and Chemical Industry Exhibits at the Paris Exhibition of 1878.

Dr. Paul was formally installed as Editor of *The Pharmaceutical Journal* in 1870, in succession to Bentley, Redwood, and Barnard, the triumvirate who had conducted it with somewhat divided counsels and policy from the time of Jacob Bell's death in 1859. From the outset of Paul's editorship the *Journal* became a weekly, and he soon introduced many of the distinctive features that it retained during the thirty-two years of his tenure of office, which witnessed many profound and pervasive changes in the internal structure and external environment of pharmacy, and consequently in the policy of the official organ of the Pharmaceutical Society. Some of these innovations were doubtless distasteful to a man who had breathed the atmosphere and been nourished on the generous aspirations and exalted ideals of the morning land of British pharmacy; and, for one of his perfervid intensity of conviction, it must have been increasingly difficult to subdue his mind and hand to a medium in which science had to compromise with business. He scorned, however, to palter with principle, as he conceived it, and during his long life, both in his editorial capacity and later, he staunchly and steadfastly held out for the prime necessity of the systematic and progressive education of the pharmacist as the only sound basis and sanction for his claim to professional recognition, and insisted on the practical value of a regular apprenticeship, as alike a preventive and cure of many of the more grievous evils from which British pharmacy suffers. In these respects the recent trend of events has amply justified his prescience.

Dr. Paul was an accomplished and versatile linguist, widely travelled, with an intimate knowledge of Continental life and thought, a brilliant conversationalist, an artistic *raconteur* of remarkable histrionic power, with a wonderful gift of playful or poignant wit, and was cast in the heroic, combative mould, with elements of sweetness and light in his composition which made him one of the most chivalrous and magnanimous of men, as ready to take a manly foeman to his arms as to break a lance with him. Dr. Paul touched life on many sides. His affinities with the modern spirit in literature and art brought him into sympathetic contact

and close communication with Dante Gabriel Rossetti and the protagonists of the pre-Raphaelite brotherhood, and Freemasonry as another aspect and manifestation of fraternity and fellowship strongly attracted him.

When Dr. Paul resigned the editorship of *The Pharmaceutical Journal* in 1902, although reckoned by the efflux of time he had exceeded the allotted span, he was still a man of vibrant vitality and unquenched spirit, and throughout his declining years had enjoyed wonderfully good health and an unabated zest of life.

RUFUS DANIEL PULLAR.

BORN JULY 6TH, 1861; DIED SEPTEMBER 22ND, 1917.

RUFUS DANIEL PULLAR was the elder of the two sons of the late Sir Robert Pullar. Born in Perth in 1861, he was educated, first at Sharp's Institute, Perth, and then at Craigmont School, Edinburgh. While still residing at Craigmont, he commenced to study chemistry at the University under Professors Crum Brown and Stevenson MacAdam. Here he made good progress, and at the completion of the course spent a year at his father's works in order to acquire a knowledge of practical dyeing.

In 1880 young Pullar entered the newly-created dyeing department of the Yorkshire College, now the University of Leeds, then in charge of the late Professor Hummel, with whom, indeed, he took up residence. He proved himself a hard-working and zealous student, and the University records state that he not only took the first prize and certificate in chemistry and dyeing, but also the highest honours and silver medal at the examination of the City and Guilds of London Institute in wool dyeing.

During the period of his stay in Leeds his kind and genial disposition found him many friends, and he enthusiastically entered into such sports as were then in vogue, being especially proficient in lawn tennis. He was, moreover, a clever photographer, and many prints are still extant from negatives taken by him during his year of studentship at Leeds. His interest in his old College and the subsequent phases of its development as part of the Victoria University and later as the University of Leeds, remained with him up to his death, and it was rarely he came to Leeds without visiting its dyeing department, so that he might discuss not only novel points of scientific interest, but also the possibility of methods for improving the study of his subject. His election in 1909 as a member of the Leeds University Textile and Dyeing Committee gave him much pleasure, and he often regretted that circumstances did not permit of his more frequent presence at its deliberations. It

was in 1882 that he took up the position of chemist to his father's firm, Messrs. J. J. Pullar and Sons, and now his real business career began. This well-known works was founded in 1824 by his grandfather, James Pullar, but its great development took place after 1848, when Robert Pullar, afterwards Sir Robert, became a partner. As chief chemist, Rufus Pullar continued until 1886, when he was received into partnership, and from that time forward his energies were so fully occupied in the development and enlargement of the business that his opportunities for actual chemical experiment became more and more limited. On the othe hand, his powers of organisation now came fully into play, and realising as he did the necessity of scientific methods, he spared no pains that these should be extended as far as possible throughout the factory. To further this object he visited foreign dye-works both in Germany, France, and America, and to these he had ready access, as a result of old family friendships which had originated with his grandfather. From its inception his firm, indeed, had closely watched each step in the advancement of the art of dyeing, and it was in these works at Perth that young Perkin, in conjunction with Robert Pullar, carried out the first experiments on any scale as to the application of mauve to fabrics. There are still in existence specimens of silk dyed with mauve at or about that time, much valued by both families, taken from a dress-length of heavy moiré silk which was presented to and graciously accepted by Queen Victoria.

As early as 1880 Pullar was elected a Fellow of our Society, and in the same year joined the Society of Chemical Industry. In 1883 he became a member of the British Association, at the meetings of which he was frequently present, and he indeed accompanied his father and uncle on its visit to Canada and the United States. His connexion with the Society of Dyers and Colourists dates from 1884, and of this in 1914 he became President, a position which he filled with distinction for two years.

From 1895 onwards Sir Robert and Mr. James Pullar, the older members of the firm, gradually withdrew from the actual management of the business, and as a result Rufus Pullar's active participation in scientific meetings, at no time an easy matter for him, owing to the distance of his home from their centres, was now considerably curtailed. Happy though he was in his own business sphere, in which, of necessity, his main interest centred, he never appeared better pleased than when in scientific circles, and there can be little doubt that he regretted that the exigencies of his position did not permit him actively to investigate some at least of the many theoretical problems which so frequently came to his notice. Whenever opportunity occurred, he spared no pains to emphasise the necessity

of a thorough scientific training for all those who were desirous of, or about to accept, positions of any responsibility in our factories, for, knowing the German methods so well as he did, he viewed with alarm the general neglect and lack of enthusiasm for science in this country. This was the tenor of his address to the Society of Dyers and Colourists in 1914, on which occasion he also pointed out that the chemist, to be thoroughly successful, should not specialise entirely in his own science, but should have also a general acquaintance with physics, engineering, and mathematics. In 1914 he accepted with much pleasure the invitation to join the Board of Trade Committee, then being formed to consider the methods of improving the dye industry in this country, and when, as a result of its deliberations, British Dyes, Limited, was founded, his interest in the matter was unceasing, and at times he visited the factory site to watch the developments there in progress.

As the head of the large and important business at Perth, Rufus Pullar was fully alive to his many responsibilities, and in addition to his desire for the continued success of the works, was keenly anxious, as, indeed, were his father and uncle before him, to devise methods for the greater comfort and social betterment of the firm's employees. Thoroughly businesslike and punctual in his habits, he expected the same from others, but, on the other hand, no calls on his leisure moments did he regret when these could be spent for the benefit of the community of his native town. Even with those who knew him intimately he rarely discussed his own concerns, and his quiet and unassuming manner gave little indication of his exceptional activity.

Although his business engagements were very exacting and his scientific interests absorbing, there are few, if any, of the numerous philanthropic institutions existing in Perth with which he had not been connected, either as president or in some position of active responsibility. He had always, indeed, been particularly attracted by public work, and he had hoped later on, as others came forward who could relieve him of his business cares, to devote himself to public life and, if possible, to enter Parliament.

At the outbreak of the war he fully recognised the necessities of the situation, and actively participated in the various local schemes which arose at this period of the national difficulty. Thus, when Lord Derby's recruiting scheme was started in 1915 he became a member of the Perth Advisory Committee, and this position he filled until March, 1916, when he was transferred to the Perth Appeal Tribunal. Later again, in 1917, he agreed to become the Sub-Commissioner for Industry in Perthshire, under the National Service scheme, the duties of which, arduous though they were, he took up with much enthusiasm, and was bitterly disappointed when,

as time went on, this movement proved a failure. In 1916 he assisted in the formation of "The Association of British Chemical Manufacturers," and although not a manufacturer himself, ultimately became a member of its Council. It is probable that the frequent journeys to London in connexion with this and the Association of Chemical Industry, together with the worry involved by the troublous crisis which had arisen in his own factory, overtaxed his strength.

He died in Edinburgh on September 22nd, 1917, after a short illness at the early age of fifty-six years.

Mr. Rufus Pullar married a daughter of the late Robert Morison, of Perth, who survives him. He leaves two sons, Mr. R. Morison Pullar, who is director and secretary of the firm, and Captain J. Lindsay Pullar, of "The Black Watch," who is serving in France.

A. G. PERKIN.

WILLIAM JAMES RUSSELL.

BORN MAY 20TH, 1830; DIED NOVEMBER 12TH, 1909.

IT is practically impossible to convey to a new generation any satisfactory impression of those features of a man's character and personality which were most apparent to his contemporaries. Hence it is of little use, and only for the satisfaction of those contemporaries, a rapidly dwindling company, that any reference is made to his genial presence, his characteristic hearty laugh, his sober and trustworthy judgment in business, and his quiet but persistent interest in matters scientific. Who he was and what he did can fortunately be set down with considerable accuracy and completeness, for documents remain which give all the necessary information. Few who knew Dr. Russell would have thought him likely to be one of those who not only made entries in a diary for the purpose of keeping engagements, but who set down every event in his own career from the age of fifteen to within a week of his death, and that all these memoranda should have been preserved.

William James Russell was born in May, 1830, and enjoyed the advantage of living under the care of father and mother during the whole of his early life, and therefore, although there is no record of his childhood, it seems certain that he received an enlightened kind of education. He went to two private schools, namely, Dr. Wreford's at Bristol and afterwards the Rev. Samuel Bache's at Birmingham. At this time, some idea of choosing for him the profession of engineering seems to have been introduced into the mind of his parents by several friends, and it was even

suggested that he should go as pupil to Mr. Beamish, a railway engineer. His father having been a good deal in Paris, had in 1801—3 attended the lectures of eminent men of science, particularly of the chemist Vauquelin, and it seems probable that the display of his interest in such subjects may have led the boy to think of the serious pursuit of chemistry as a life-long occupation. Moreover, he may have been influenced to some extent by tradition in the family concerning his father's, and especially his grandfather's, association with the famous discoverer of oxygen, Joseph Priestley. Whatever may have been the original source of the influence which ultimately determined his career, the diary reveals the fact that at the age of fifteen or thereabout he was not only attending various lectures on geology, botany, and chemistry, but was lecturing himself either to schoolfellows or friends, probably the latter, as the entries appear to have been made in the holidays. On September 23rd, 1847, the entry is "Left Birmingham for good," and on October 13th following, "Came to London," and next day, "Began to attend the classes." This was at University College, London, where he became a student of chemistry under Graham and Williamson.

Though doubtless a man's career is subject to much modification by the conditions surrounding his life, there is at least as much to be attributed to the bias which he receives from his ancestry; and before proceeding further, a glance may be appropriately taken at the history of the strange and eventful lives of his father and grandfather long before his birth. This has been provided in an interesting volume, "The Russells of Birmingham in the French Revolution and in America, 1791—1814," by S. H. Jeyes (George Allen and Co., 1911), which has been compiled from letters and especially from the diaries kept by Martha Russell, elder of the two aunts of William James.

Russell's grandfather, William Russell (1740—1818), was a contemporary and friend of Joseph Priestley, the famous divine and discoverer of oxygen. At the time of this discovery, William Russell was thirty-seven years of age, and must have felt considerable curiosity about his friend's work and its results, especially as, in a sort of way as guardian and warden of the Assay Office in Birmingham, he was presumably acquainted with some applications of such practical chemistry as were known in his day. But the tie of sympathy between the two men was rather political and religious, Russell being a member of the Unitarian congregation presided over by Priestley, and a substantial supporter of the minister, not only as a member of his congregation, but by furnishing liberal supplies of money. This association with so notorious a reformer, for

whom the High Church party of the day had no better name than "atheist" and "revolutionary," led to unfortunate consequences.

Public feeling in this country was exacerbated to a high degree by the outbreak of the French Revolution, and a series of disorders broke out in Birmingham, in the course of which Priestley's house was burnt and all his apparatus destroyed on July 14th, 1791, and the house of William Russell at Showell Green met with the same fate two days later. Priestley fled to London, and in April, 1794, he sailed for America and settled at Northumberland, a small town in Pennsylvania, where he died in February, 1804.

William Russell, though evidently a man of considerable courage and determination, having more than once confronted the rioters with remonstrances, was ultimately induced to seek a new home across the Atlantic. The story of the adventures of the father with his two daughters Martha and Mary and his son Thomas Pougher is recorded in the diaries of the elder daughter. To the volume already mentioned the reader must be referred for details, which, it must be said, possess more than a mere personal interest, as they throw much light on the state of parties in this country, on the condition of France during the Revolution, and on the social conditions prevailing in America. It is sufficient to say here that William Russell and his family started from Gloucestershire in July, 1794, and drove to Falmouth, where on August 13th they embarked. They had been at sea only a few days when they encountered a French frigate, and all the English voyagers were captured and taken to Brest. After some months they were released, and made their way to Paris, where they stayed until the following summer, when they sailed from Havre, and ultimately landed in New York in August, 1795. William Russell, ardent Republican though he was, found little to satisfy him in America, and in a few years the whole family returned to Europe.

Thomas Pougher Russell, the only son of William Russell, born February 3rd, 1775, was some years younger than his sisters, who were born respectively in 1766 and 1768. He seems to have found life in the new country less tolerable than did his more accommodating sisters. His father had purchased considerable property in France, and in 1801 he retired to his estate near Caen. Thomas spent a good deal of time in Paris, but there were difficulties about personal intercourse between father and son owing to the continuance of the war and the anomalous political position of the father. William Russell was admitted to the rights of French citizenship in 1807, and two years later Thomas also became a French citizen.

In 1813 Russell sold part of his French property, and advantage was taken of the peace which temporarily followed the internment

of Buonaparte in Elba for both father and son to return to their native country. No record exists of the terms on which Russell made his peace with the English authorities, but it is pleasant to know that he was spared to live four years in his native land. On January 26th, 1818, he died at the house of his son-in-law, James Skey, at Upton-on-Severn, aged seventy-eight, "a long suffering man who had met all his troubles with a cheery spirit and indomitable courage."

From the volume referred to, we learn that Thomas Pougher Russell maried in May, 1817, Mary, daughter of James Skey by his second wife, Eleanor (*née* Brockhurst), and had issue two daughters and one son, named after his two grandfathers William James. For the last thirty years of his life Thomas Russell was a banker in Gloucester, in partnership with James Skey and others. This private bank afterwards became the Gloucestershire Banking Company, of which he was a director. He also served for many years on the committee of the Gloucester and Berkeley Canal, and died in 1851 at Gloucester, of which city both he and his son were freemen.

As a student in University College, young Russell had the advantage of working under the most distinguished chemists of his time and of meeting with congenial companionship. Thomas Graham was the professor until his retirement on becoming Master of the Mint in 1855. At this time he was occupied with his famous studies of the phenomena of liquid diffusion. George Fownes was still professor of practical chemistry, but he died in January, 1849, and was succeeded by Alexander Williamson in October of that year. Russell's diary states that he began quantitative analysis in January, 1848, doubtless under the direction of Fownes, but as the diaries are missing for above a year at this time, there is no record of his associations with that brilliant man. On April 30th, 1850, "Heard that I had the medal for the Chemical Essay" is the entry. Other notes show that he went to hear Faraday lecture, and that on May 6th, 1850, he "went with Mr. Watts* to the Chemical Society to hear the discussion between Frankland and Hofmann about ethyl, amyl, etc."

Russell was not content with listening to discussions, for on the 29th of the same month, "Had a discussion at the Birkbeck Phil. Soc. whether Priestley or Scheele was the greatest philosopher. I spoke for Scheele; discussion adjourned." And again, in November, "Opened the discussion on the Dr.'s new theory of etherification at the Birkbeck Philosophical Soc." But all was not science and work, for there are many entries of dances and

* Henry Watts of Dictionary fame.

dinners, and especially of visits to theatres; among the last, November 11th, 1850, "Went with Frank and Henry Roscoe to the Olympic Theatre to see Miss Faucit," etc. This was the end of his student time at University College, for in January, 1851, Frankland, who was then at the College of Engineering at Putney, offered him the post of assistant at Owens College, Manchester, then about to be opened, and where Frankland had been appointed the first professor of chemistry. On February 8th, 1851, his father died, and naturally this event took him away from his work for a time; but by the end of the month he was in Manchester assisting Frankland with his lectures, the introductory lecture being given on March 20th. Here Russell remained until 1853, when he decided to go to Germany.

July 1st: "The laboratory students met and presented me with a copy of Tennyson's works as a parting gift, a most pleasing and unexpected thing to me."

The choice of the laboratory at Heidelberg, where Bunsen was professor, was determined on before the end of the previous year, for a letter from Roscoe dated December 14th, 1852, contains the following passage: "I am glad that you think of Heidelberg first, because I have a great desire to go there too, and I am sure Bunsen must be a capital man." Early in September Russell arrived at Heidelberg, and on the 7th "Harry Roscoe and I went to see the laboratory, a curious old place very different from the Owens College one." Among his fellow-students were, besides Roscoe, Ronalds and Matthiessen, Lothar Meyer, Edmund Atkinson, Pauli, Hermann, and Meidinger. Experiments on paraffin, which he had begun at University College, were carried on for a time, but soon Bunsen suggested other work, and on December 16th, 1854, the diary reports, "Took my degree." Whether the subject of his thesis was the composition of the gases produced in flames or the research on a method of estimating sulphur in volatile compounds (published in the *Quart. Journ. Chem. Soc.*, 1854, **7**, 212) is uncertain. He seems to have remained at Heidelberg until the following August, when he returned to London.

After various disappointments and tentative experiments in connexion with industrial applications of chemistry, Russell became teacher at the Midland Institute, Birmingham, and gave a short course of lectures in June, 1857. This summer the professorship at Owens College, Manchester, fell vacant by the removal of Frankland to London. Russell became a candidate, but his friend Henry Roscoe, his senior by three years, received the appointment. Russell returned at the end of the year to University College, and on December 7th "went to the laboratory, saw Williamson, and

he explained his gas apparatus to me; the thing is altogether in an impracticable form." This, however, was followed by a long investigation, which resulted in two papers jointly with Dr. Williamson (*Proc. Roy. Soc.*, **9**, 218; *Journ. Chem. Soc.*, 1865, **18**, 238), and two others independently, on gas analysis and on the application of the measurement of gases to quantitative analysis (*Journ. Chem. Soc.*, 1868, **21**, 128, 310). While this work in the laboratory was going on, Russell conducted the evening classes in chemistry at the college, and gave a course of practical chemistry in the school. During the first session of the Albert Veterinary College, he gave the course of lectures on chemistry, and in July, 1860, was appointed lecturer on natural philosophy at the College for Ladies, Bedford Square (Bedford College). He was now pretty fully occupied with teaching, but it did not prevent activity in other directions. He had attended several meetings of the British Association, and at the Oxford meeting in 1860 Russell took a leading part in the foundation of the famous dining club, known as the "Bs." An interesting account of some of its proceedings was given in Dr. Scott's Presidential Address, March, 1916 (T., **109**, 342). The diary tells us that the rules of the club were drawn up on July 23rd, "the first meeting of our dining society" was on November 6th, and another meeting took place at the Cheshire Cheese on December 4th.

In October, 1861, Russell became engaged to Fanny Follett Osler,* a daughter of Abraham Follett Osler, the well-known glass manufacturer, of Birmingham. They were married on August 21st following, and took up their abode at 8, Circus Road, St. John's Wood. In 1865 he was appointed lecturer at the Royal Albert Veterinary College, and in the following February he bought the house 34, Upper Hamilton Terrace, which remained his London home to the end.

In 1868 Russell was appointed to the post of lecturer at St. Mary's Hospital, previously occupied by Matthiessen, and his activity may be estimated by recalling the facts that during the seven or eight years immediately previous to this time he had continued his teaching at University College and at Bedford College. He also attended meetings of the British Association, and on the last two occasions had served as one of the secretaries of the Chemical Section. He worked assiduously at gas analysis, and in conjunction with Williamson published several papers on the subject in the Proceedings of the Royal Society and in the Journal of the Chemical Society. He had also investigated jointly with Matthiessen the important question as to the cause of the

* She died on May 15th, 1871, leaving a son and a daughter.

vesicular structure of copper. They showed that this phenomenon is observed when copper is melted under charcoal only when oxygen or air is passed through the metal, and they inferred that the peculiar structure could only be attributed to the formation of carbonic oxide arising from the reduction of cuprous oxide within the mass by charcoal. The cavities in the metal are always untarnished, and hence cannot contain any oxidising gas. In 1863 he had communicated to the Chemical Society some important work on the atomic weights of cobalt and nickel, and was led to the conclusion that they are practically identical, the value found for Co′ being 29·370, whilst that for Ni′ was 29·369. The method consisted in the reduction of the protoxides by hydrogen and determination of the weight of the resulting metal. In 1869 he published further experiments, in which the same metal used in the former work was dissolved in dilute hydrochloric acid, and the evolved hydrogen was measured. The results were practically the same, and the atomic weights of the two metals were consequently supposed to be represented by the same number, namely, 29·3 or thereabouts. This was in accord with the view prevalent fifty years ago, even after the discovery of the periodic law. The problem presented by these two closely allied elements, however, attracted a large number of chemists, and the idea of the identity of their atomic weights has had to be abandoned. This may perhaps be partly attributed to advance of knowledge as to the properties of the two elements, including the discovery of nickel carbonyl, the decomposition of which affords a means of separating that metal completely from all other substances. There can be no doubt now that the atomic weight of cobalt is greater than that of nickel, and practically in the ratio given in the International Table of Atomic Weights, namely, Co : Ni : : 58·97 : 58·68, when O = 16. These values agree with the result obtained by comparing the specific heats, namely, 59·01 : 58·70. At St. Mary's Hospital, Russell remained about two years, but in December, 1870, he was appointed to the lectureship at St. Bartholomew's, left vacant by the unhappy death of his friend Matthiessen. A new laboratory had been very recently built and had been ready for occupation at the commencement of the session in October. Here Russell continued his work until he retired from all teaching in 1897.

A word may here be said on the subject of Russell's qualities as a teacher. He was wise enough to perceive that the course of elementary chemistry usually followed was unsuitable for medical students without modification, and the change he introduced undoubtedly affected the course of instruction in other medical schools

and the syllabuses of examinations, such as those of the Conjoint Board. All this led to great improvement in the attitude of the students of medicine toward the chemical subjects, for whereas there had been previously not only reluctance to attend, but frequent disorder, they soon recognised the sympathy of their present teacher, and there was little, if any, trouble during his connexion with the school. The diary gives evidence on this point, for on January 11th, 1871, the entry is: "Gave my first lecture at Bartholomew's; went off all right," and on the 14th: "Lectured again; students perfectly quiet." As to other difficulties consequent on the many changes which about that time arose not only in the requirements of the medical curriculum, but also in the working of the School itself, we have the testimony of Dr. Samuel West, who was then working in the laboratory with Russell, that they were met "with invariable good humour, willingness, and courtesy." He seized the opportunity of becoming President of the Chemical Society to deliver in 1890 an address setting forth his views on the teaching of chemistry to students of medicine. These were inspired with his characteristic good sense. But it was not only in relation to medical students that his interest and sympathy were engaged. He had great experience as a teacher of elementary chemistry and physics to young people, both at University College School and at Bedford College, and after retirement from the lectureship at the latter institution he became chairman of the Council and took an active interest in the development of the College. Part of his success as a teacher and examiner probably arose from the habit of his mind, which was more attracted by facts and phenomena than by theories concerning them. He was certainly not one of those who delight in the manufacture of hypotheses, and all his own work and teaching were directed by unaffected good sense and clear judgment.

In 1872 Russell was elected F.R.S. He was elected into the Royal Society Club on June 26th, 1879. In 1873 he was president of the Chemical Section of the British Association at Bradford. His address was chiefly devoted to the very appropriate subject of alizarin, the history of the discovery of its constitution, and of the then recent synthetical production of this important colouring matter.

The *Journal* of the Chemical Society contains, in January, 1874, a very interesting paper on the action of hydrogen on silver nitrate, in which it is shown that hydrogen passed into a silver nitrate solution causes the deposition of metallic silver in quantity equivalent to the hydrogen which is absorbed, provided the solution is prevented from becoming acid by introducing a small quantity of silver

oxide. If the liquid becomes acid in consequence of the displacement of the silver, nitrous acid is formed and the reaction becomes more complicated.

About the same time experiments had been going on in his laboratory on a method of estimating urea in urine for clinical purposes, and in August, 1874, the *Journal* contains a paper on the subject published jointly with Dr. S. West. The method was based on the action of hypobromite on the fluid and measurement of the evolved gases. This was followed up in the wards of the hospital, and in 1880 the authors published their results in the *Proceedings* of the Royal Society (No. 204, 1880).

Various other researches were carried on, and at the same time Russell became involved in several technical inquiries which took up practically all his spare time. In 1875 he was also appointed one of the examiners in chemistry to the University of London. His colleague for some time was Roscoe, and naturally the London man got his full share of the work and the attendances at examiners' meetings. In 1876, also, the movement began within the Chemical Society which resulted in the formation of the Institute of Chemistry, and Russell's attendance at several initiatory meetings is recorded in the diaries. He became president of the Institute in 1893, and served for three years. About this time the subject of absorption spectra attracted his attention, and he spent much time working with Professor Lockyer at South Kensington. The result was a paper in the *Proceedings* of the Royal Society, 1880, on the absorption spectra of cobalt salts. But more important results were published (in conjunction with W. Lapraik) the next year on "Absorption Bands in the Visible Spectrum produced by Certain Colourless Liquids." Hartley and Huntington had already studied the absorption in the ultra-violet (*Proc. Roy. Soc.*, 1880, **28**, 233), whilst Abney and Festing had observed the absorption in the infra-red end of the spectrum produced by colourless liquids (*Proc. Roy. Soc.*, 1881, **31**, 416), but the visible portion of the spectrum had not previously been examined, and the discovery of bands in this part of the spectrum produced by the alcohols and colourless hydrocarbons has led to a vast amount of work by others since that date. The study of absorption spectra interested Russell very much, and there was another paper, also in conjunction with Lapraik, in the *Journal* of the Chemical Society (1882) on chlorophyll," but, as he himself stated, the expectations which had been raised and the hopes entertained when absorption spectra began to be studied were not then fulfilled; nor can it be said that they have been since. This, however, cannot be regarded as an argument against carrying on such investigations; rather the

contrary, for inability to deduce definite conclusions merely indicates a state of imperfect knowledge.

All kinds of problems which possess a direct practical interest or value always attracted Russell, and this led him to devote a great deal of time to the examination of the air and rain of London. St. Bartholomew's Hospital Report (Vol. XX.) contains a record of work done in 1882–3 on the carbonic acid in London air, whilst the Meteorological Office Report for August, 1885, gives the results of a laborious inquiry into the nature and amount of the impurities, solid and gaseous, in London air.

Another subject which occupied much time and attention was the study of the action of light on water-colours undertaken in conjunction with Sir William Abney at the request of the Science and Art Department in 1886. The first report was issued two years later, and contains an elaborate scientific discussion of the nature of colour and the constitution of various lights to which water-colours are exposed, as well as the influence of moisture and air and the extent of the chemical changes observed. The conclusions to which the investigators came may be briefly summarised in the statement that mineral colours are far more stable than vegetable colours, that moisture and air together are essential to the production of change, and that it is the blue and violet components of white light which are chiefly concerned in bringing about fading in the pigment. One of the difficulties of the inquiry arose from the fact that one of the main objects of the investigation was to ascertain what changes water-colours would be liable to if exposed to usual indoor conditions during at least an ordinary working lifetime. Fortunately, twenty-six of the colours originally subject of inquiry had been preserved by Mr. T. H. Russell in his father's house, and in 1914 they were examined by himself and Mr. Edwin Bale, R.I. The results of their examination are recorded in the *Journal* of the Imperial Arts League, and have been reprinted in the form of a pamphlet, which has been published by Messrs. Winsor and Newton, Ltd., so that artists can select for themselves the colours which are known to be the most durable.

An inquiry of cognate character was directed as to the state of the Raffaelle Cartoons at South Kensington. This Russell reported on in July, 1891. Ancient Egyptian pigments were also the subject of a lecture he gave at the Royal Institution in March, 1893.

It is time, however, to refer to his long connexion with the Chemical Society, of which he was elected a Fellow on March 3rd, 1851 (before he was twenty-one years of age), and of which forty years later he became president. Absence in Germany and at Manchester sufficiently accounts for the fact that the diaries give no evi-

dence of his attendance at the meetings for several years after election, but from 1857 onward he seems to have attended frequently in every year without a break down to the year of his death. In 1863 he first joined the Council, and thereafter he was an active member of various committees connected with the Society. He was elected Treasurer in 1876, and held that office until elected President in 1890. The great event during his occupation of the chair was the celebration of the jubilee of the Society, in 1891. As President, Russell took the chair at the dinner on February 25th, 1891, and the occasion was distinguished by the presence of the Prime Minister, Lord Salisbury. The diary characteristically reported that "it went off very well."

A series of experiments undertaken with the object of repeating Becquerel's observations on the photographic effects produced by compounds of uranium resulted in the remarkable discovery that zinc and a number of other metals produce a similar effect. The first announcement of the fact appeared in the *Proceedings* of the Royal Society for 1897. And the prosecution of the work led to the further discovery that not only metals, but varnishes, printing ink, and a variety of organic substances share this property. The results were collected in a second paper, which formed the Bakerian Lecture for 1898. The effects were soon traced to the formation of hydrogen peroxide, and in March, 1899, a third paper was communicated to the Royal Society under the title "Hydrogen Peroxide as the Active Agent in producing Pictures on a Photographic Plate in the Dark." One remarkable point brought out in these experiments was the exceedingly minute quantity of the agent which was competent to produce the effect. The inquiry was pursued for some years, and the effects on a photographic plate produced by sections of various woods provided a fascinating subject, which was developed with many beautiful illustrations and communicated to the *Philosophical Transactions* for 1904. Two later papers described the effect produced by leaves and other parts of plants, also by resins. In 1897, Russell had resigned the office of lecturer at St. Bartholomew's Hospital, which he had held for so many years, and after this time his experimental work was done at the Davy-Faraday Laboratory. Here, also, he carried out the experiments on the "Formation of Definite Figures by the Deposition of Dust," which were published in the *Philosophical Transactions* for 1903. An explanation on physical principles of the formation of these curious deposits was soon afterwards given by Mr. J. Aitken, F.R.S. (*Proc. Roy. Soc.*, 1904, **72**, 211).

Russell was elected under Rule II a member of the Athenæum Club on February 26th, 1889. The rule provides for the annual

introduction of a small number of "persons of distinguished eminence in science, literature, or the arts, or for public services." A few years later Russell became a member of the Committee.

Russell delighted in the country and in all sorts of natural objects and in scenery. He had travelled a good deal on the Continent of Europe, but his own country supplied him with all the enjoyment he needed in his latter years. And he was a most genial host. For many years, from about 1882, he had a house on the edge of Dartmoor, Scorhill, near Chagford, and there he delighted to show his visitors the views of sunsets over the moor or the curiosities of form among the tors. Notwithstanding its attractions, the difficulty of access to this retreat led to a removal in 1897 to St. Ives, near Ringwood, Hants, a house surrounded by beautiful plantations, including extensive rhododendron avenues. Here he entertained frequent visitors, and the annual excursion into the neighbouring New Forest at Whitsuntide was an event for pleasant anticipation. It was delightful to accompany him in visiting his favourite trees in his own grounds, and to share the evident enjoyment with which he discoursed about their history or peculiarities.

In August, 1909, he left London as usual, and went to St. Ives. He had, however, been failing in physical strength for some time, and though in the early part of the summer he had dined out several times, there is an entry in the diary on July 18th, "Taken ill," and on August 10th, "Went to Ringwood." Here, after a short illness, during which he was unconscious, he passed quietly away.

W. A. T.

FRANCIS SUTTON.

BORN FEBRUARY 19TH, 1831; DIED APRIL 16TH, 1917.

THE name of Francis Sutton is known throughout the chemical world by reason of his authorship of "A Handbook of Volumetric Analysis," which has been recognised as the standard work on the subject for the past fifty years. Ten editions of the work were published during the author's life, and each edition has kept well abreast of the current work in this branch of analysis. Sutton contributed but little original matter to analytical chemistry; his strenuous life and professional engagements never allowed him time for development in this direction, although his natural ability and grasp of the science might, in other circumstances, have enabled him to become a great chemist.

Francis Sutton was an only son, born on February 19th, 1831, at

Great Plumstead, a village near Norwich, Norfolk. His father, Francis Sutton, was a small farmer and farrier with a local veterinary practice. The son received his earliest education at the village school of Blofield, two miles distant from his home, and later attended a private school in Norwich, riding daily the ten miles to and fro by pony.

At the age of fourteen young Sutton was placed with a Mr. Harper, a druggist, of Norwich, with a view to acquiring some knowledge of drugs and chemicals prior to being sent as a student to the Veterinary College in London, for his father intended the boy to become a veterinary surgeon. The study of materia medica, botany, and chemistry was found so interesting that with his father's consent he was apprenticed to Mr. Harper and remained with him as assistant until 1851.

Then, at the age of twenty, Sutton decided to join a former fellow-apprentice who had started a druggist's business in West Clayton Street, Newcastle-on-Tyne, and it is of interest that the journey to the northern town was made by sea in a small coasting vessel from the now dead port of Blakeney on the north Norfolk coast. Thus he was brought into contact with a then growing centre of chemical industry and study, and while practising pharmacy had opportunity of becoming acquainted with men interested in pure and applied chemistry, among others Joseph Wilson Swan and John Pattinson, who remained life-long friends. A Dr. Glover, a physician of Newcastle, who devoted a good deal of time to medical chemistry and analysis, and subsequently became physician to the Royal Free Hospital, London, took much interest in the young pharmacist of West Clayton Street, lending him books, employing him in various chemical experiments as an assistant, and advising him to take up seriously the study of scientific chemistry. As a result of this help and encouragement, Sutton, in such time as was available, attended the lectures and worked in the laboratory of Dr. Richardson, then lecturer in chemistry at the Newcastle College of Medicine—at that early date associated with the University of Durham, and later known as the University of Durham College of Medicine. It was, however, through Dr. Marreco, then assistant to Dr. Richardson, that he received his main instruction in the theory and practice of chemistry, and laid a firm and sure foundation for his subsequent interest and achievement in that science. He must have been an apt and earnest pupil, for, as junior partner in the druggist business, most of the day was fully occupied, and his lectures and laboratory work had to be snatched at odd hours.

His residence in Newcastle and the opportunity for instruction

came to an abrupt end in November, 1854. His old master at Norwich was dying, and an urgent appeal was made to Sutton to return to Norwich and manage the business in which he had served his apprenticeship. He did so, and settled in Norwich, carrying on the pharmaceutical business in partnership with his late master's widow, and subsequently alone, until growing interests necessitated taking a partner. Meanwhile his keen interest in chemistry and chemical analysis was maintained, and led to part of the business premises being converted into a laboratory. At this period the work of Lawes and Gilbert at Rothamsted in the use of artificial fertilisers was beginning to receive the attention of agriculturists, and Sutton turned to the study and analysis of fertilisers. By advocating the new ideas among local farmers and advising and helping them, he established the nucleus of an analytical and consulting practice, which quickly developed.

In 1870 he originated and became managing director and partner in a chemical manure works at Runham, Great Yarmouth (Baly, Sutton and Company, Ltd.), where the manufacture of sulphuric acid, hydrochloric and other acids, as well as superphosphates, chemical manures, and sulphate and chloride of ammonia was carried on. The works and business were disposed of in 1893 to Messrs. Prentice Brothers, Ltd., of Stowmarket.

While at Newcastle in 1853 Sutton had become a member of the Pharmaceutical Society, and in Norwich his ability as a pharmacist was quickly recognised. He was elected to the Council of the Pharmaceutical Society in 1870 and continued to serve until 1876, when he finally abandoned pharmacy and disposed of the business to his then partner—in order to devote his time to his consulting and analytical practice and other interests. While serving on the Council of the Pharmaceutical Society he was chosen as one of the two delegates to represent Great Britain at the International Pharmaceutical Congress in St. Petersburg in 1874, and was afterwards elected a corresponding member of the Imperial Pharmaceutical Society of that city and also of the Apotheker Verein of Vienna.

Sutton's earliest contribution to scientific literature was in the form of two papers, published in the *Chemical News* in 1860, on the volumetric determination of phosphoric acid by uranium. In 1862 the first edition of his "Volumetric Analysis" was published; it was a small volume of 273 pages; the second edition followed nine years later in 1871, and was much more ambitious and comprehensive. Professor H. McLeod contributed a section on gas analysis, and the late Mr. William Thorp contributed to the section on water analysis. The latter, by advice and correction of proofs, gave acknowledged assistance in many subsequent editions.

The fourth edition was translated into French by the late Dr. C. Méhu and published in Paris in 1883. In all, ten editions were published in Sutton's lifetime, the last being edited by his son, W. Lincolne Sutton, and A. E. Johnson.

The period of life between 1860 and 1876 was an exceptionally full one, for Sutton, while carrying on simultaneously a very successful pharmaceutical business, had established and developed a considerable analytical and consulting practice, published the first and larger subsequent editions of his book, and had founded and was managing the chemical works at Yarmouth He had been appointed analyst and consulting chemist to the Norfolk Chamber of Agriculture, public analyst for the County of Norfolk and Borough of Great Yarmouth, and gas examiner to the City of Norwich. For many years he was in considerable demand as an expert witness before Parliamentary Committees and in the Law Courts.

Francis Sutton undoubtedly possessed great natural ability and versatility and had wide interests. In his prime he was a strikingly handsome man, with finely moulded head, aquiline nose, full beard, and ruddy complexion. His generous nature, sociability, and love of "good company" endeared him to a wide circle of friends; another personal trait was his beautiful handwriting. He took an active part and held office in various local scientific and other societies, such as the Norfolk and Norwich Geologists' and Microscopical Societies (both now extinct), the Norfolk and Norwich Naturalists' Society, of which he was at one time president, and he was an original member of the Norwich Science Gossip Club. He was a great lover of music, and possessed considerable knowledge of classical and operatic music. He was an active member of the Norwich Philharmonic Society for over forty years, and played the clarinet and later the oboe in the orchestra. He served for many years on the general committee and committee of management of the Norfolk and Norwich Triennial Festivals. He was an omnivorous reader of catholic taste, and served for many years on the committee of the Norfolk and Norwich Library, some time as president. Throughout his long life his chief outdoor recreation was fishing, a sport in which he took general interest. He was appointed a juror to the original Fisheries Exhibition held in Norwich in 1881 and also in the International Fisheries Exhibition of 1883 held in London.

Francis Sutton married in 1859 Marianne Harriett, the youngest and eleventh child of William Lincolne of Halesworth, Suffolk, and had issue seven children, three sons and four daughters, all of whom lived to maturity and married. F. N. S.

WILLIAM HENRY SYMONS.

BORN NOVEMBER 16TH, 1854; DIED AUGUST 25TH, 1917.

THE ranks of the Public Health Official Service suffered the loss of a most capable and enthusiastic member by the death, on August 25th, 1917, of Dr. William Henry Symons, for twenty-one years Medical Officer of Health of the City of Bath.

Born on November 16th, 1854, Dr. Symons, a native of Dunster, first adopted chemistry as a vocation, and becoming chemist to Messrs. Idris and Co., aerated water manufacturers, of Camden Town, rapidly acquired a considerable practice as a consulting chemist. During this period he became a member of the Chemical Society in 1874, Fellow of the Institute of Chemistry in 1888, and published various papers, among them being: "A new method for the detection of various starches," "The detection of sodium in lithium carbonate," "Ulexine, an alkaloid from the common furze," "The difference between ulexine and cytisine," and a paper in the *Transactions* "On the volumetric determination of carbon dioxide in the atmosphere." His inclinations were, however, towards the application of chemistry to medicine, and entering St. Bartholomew's, he obtained the M.R.C.S. and L.R.C.P., and the M.D. Brussels in 1894, and the D.P.H. of Oxford and Durham in the following year. During this period he acted as assistant demonstrator in materia medica, was examiner under the Pharmacy Act, published papers on "Ipecacuanha," and edited the "Year Book of Pharmacy." For a short time he acted as Medical Officer of Health to St. George's, Southwark, and was appointed to the City of Bath in 1896. During the twenty-one years in which he held this post, he inaugurated a completely new régime with regard to the municipal health department, and his elaborate reports on the health of the city were greatly valued by the Corporation. His work in connexion with child welfare at Bath "brought this branch of public health work to a high standard of efficiency, and his efforts to secure a thoroughly satisfactory midwifery service in the city, embodying the provision of the Municipal Midwives Act, were fruitful of good results." For some years he was a member of the council of the Society of Medical Officers, and president of the West of England branch in 1911.

His interests were wide: he had made a special study of town planning, and in this connexion frequently visited the Continent; he also took an active part in the organisation of the Wensley Sanatorium, near Bath, for tuberculosis. One of his hobbies was

meteorology, and it was through his energy that the meteorological department at Bath was modernised, several stations equipped, and for the first time a series of careful observations recorded. This was obviously of value to a city famous as a health resort, and led to his appointment as City Meteorologist and a member of the Committee of the British Association appointed to investigate the effect of climate upon health and disease.

He was a well-known member and fellow of the Royal Sanitary Institute, and contributed to their *Journal* and discussions. Among his contributions, not previously mentioned, were the following: "Cancer in relation to the dwelling," "Ventilation," "The life-history of *Musca domestica*" (and it may be mentioned that he was a pioneer in the crusade against the fly danger), "Flies and refuse heaps," "Distribution of phthisis."

In the obituary notice in the *Journal* of the Royal Sanitary Institute, one of his friends wrote as follows: "One of his most striking personal qualities was his great enthusiasm in whatever he undertook . . . no one who was brought into intimate relationship with him ever harboured any unkindly sentiment towards him. The golden qualities which made him a model husband, father and friend, were somewhat cloaked by an excessive natural reserve, but these qualities were bountifully disclosed to many friends and colleagues who mourn his loss and who will be inspired by the memory of his friendship, and the earnest endeavour which secured for him the reward of much good work accomplished in the sphere of public health." F. F.

THOMAS TYRER.

BORN NOVEMBER 17TH, 1842; DIED FEBRUARY 21ST, 1918.

THE sudden death of Mr. Thomas Tyrer, which took place at his residence, 14, Sandswell Mansions, Hampstead, on Thursday, February 21st, is already generally known to the chemical world at large, and it came as a great shock to such intimate friends as the writer, who had the privilege of being one of his closest friends and was associated with him both in business and private life for some twenty-nine years.

Although of good age, there was a fair prospect of further years of useful life, but the death of Mrs. Tyrer and a recent operation for cataract evidently affected his health and tended to hasten the end.

As one who was treated by Mr. Tyrer as a son or younger brother, the writer feels that (beyond the great loss sustained by chemical industry) the world has lost a good man—one who was generous and good-hearted, always ready to acknowledge and help forward others, even at the expense of himself. Although somewhat hasty in temper (like many other great men), Mr. Tyrer never knowingly allowed his feelings to injure or hurt anyone, and as a friend and adviser would spare no trouble or expense to render the very best possible help, his help being by no means confined to those who could claim strong personal friendship. In business he was generous to all who in any way showed themselves faithful and earnest, and he had no sympathy with those who believed that in business the great and strong are justified in "ousting" the smaller and weaker man.

He was able quickly to grasp the salient points and master the details of any matter placed before him, and his sound reasoning and extensive and general knowledge made him a valuable counsellor, whilst he was also possessed of great diplomatic ability. Had he turned his thoughts towards political life he would doubtless have become one of the leading men in the government of the country.

As has already been mentioned in the various trade journals, Mr. Tyrer's connexion with commercial and industrial chemistry extended over some fifty-five years. He was born at Wolverhampton in 1842, and received his education from his father, who was a schoolmaster, from whom he also acquired his habit of fearlessly speaking the truth to all and in all circumstances where necessary.

He was apprenticed to a manufacturing chemist named Wildsmith at the age of fifteen, and he entered the Royal College of Chemistry in Oxford Street (now incorporated in the Imperial College of Science) in 1861, and studied here under Hofmann, his experience with whom and with his fellow-students being always a favourite theme for conversation.

He also studied biology under Huxley and physics under Tyndall, but owing to the condition of his finances he had to relinquish these studies and became technical manager to Messrs. May and Baker, of Battersea, of which firm he subsequently became a partner.

Meanwhile, he was acting as honorary lecturer in chemistry to a working man's institute. His partnership with Messrs. May and Baker terminating in 1889, he, on January 1st, 1890, acquired from Messrs. Dunn and Co. the Stirling Chemical Works, Stratford, which in 1898 was formed into a limited liability company

(Thomas Tyrer and Co., Limited); of this he became managing director, and held this position at the time of his death.

In 1912 he undertook the manufacture of cellon aeroplane dope, and on the outbreak of war in 1914 he was able to extend and keep pace with the demand. Later on, by the erection of one of the best equipped factories, he added largely to the output, and was able to cope with the continually increasing requirements of the Government, due to the war.

Outside his business, some of the widest known work he did was in connexion with the duty-free alcohol question and the foundation of the Society of Chemical Industry. As chairman of the Chemical Trade Section of the London Chamber of Commerce, he, in conjunction with David Howard, Charles Umney, and others, took part in obtaining the grant of duty-free spirit for medicinal and other alcoholic preparations to be sent abroad, and thus enabled English manufacturers to compete with the foreign trade in these products.

He was also successful as a member of the Industrial Alcohol Committee in obtaining the reduction of the quantity of wood spirit used in denaturing alcohol (for use in manufacture) from 10 to 5 per cent.

In connexion with the Society of Chemical Industry, which was really instituted by a meeting of chemists convened by Mr. Hargraves at Widnes in 1879, and subsequent meetings at Widnes, Liverpool, and Manchester (known first as the Widnes and Runcorn Chemical Society, and later as the Lancashire Chemical Society and the Society of Chemical Engineers), Mr. Tyrer was most active, and may be said to have been one of its principal founders. In April, 1881, a meeting was held at Burlington House, at which Mr. Tyrer, with G. E. Davies, Roscoe, Abel, Ludwig Mond, Spiller, and other famous chemists took a most prominent part, Mr. Tyrer suggesting that the society be called the Society of Chemical Industry, and this suggestion was adopted in spite of opposition. He was honorary secretary of this society for ten years, chairman of the London Section 1890—1892, president 1895—1896, and honorary treasurer from 1908 (after the death of Mr. Hall) to the date of his death.

During the whole time he served the council in every direction, and his energies in this connexion aided materially in bringing the society from a small beginning to one of the largest, the members now numbering from four thousand to five thousand. That his great efforts in the chemical industry were recognised is shown by the fact that he had many honours conferred upon him, amongst

which may be mentioned the award of a silver salver and purse of gold by the Society of Chemical Industry under the presidency of Sir Fredk. Abel in 1891, the medal of the society in 1910, and in connexion with the industrial alcohol question a silver tea and coffee service in 1905.

One might go on indefinitely describing the work of such an energetic worker as Mr. Tyrer, but the greatest thing of all is the character he leaves behind, which cannot be better expressed than by quoting Professor Henderson's recent words.

"Kind-hearted and generous; a steadfast friend and chivalrous opponent; a wise and cautious counsellor; a benevolent helper of many a young and struggling man; an earnest advocate of every cause which he believed to be right and good; eminently sociable, a lover of music, a lover of talk in congenial company—such was Thomas Tyrer. It will be long before his memory fades."

Mr. Tyrer died as he wished, "in harness," and, as Professor Henderson says, it will be long ere his memory fades, especially amongst those who knew him well and recognised his real worth.

T. TUCKER.

REGINALD COWDELL WOODCOCK.

BORN DECEMBER 11TH, 1851; DIED JANUARY 5TH, 1918.

REGINALD COWDELL WOODCOCK received his early education at two private schools, and subsequently (1866–1867) attended King's College School, London, taking the regular course in French, German, drawing, chemical physics, etc.

During 1867–1868 he was employed in Paris by the London Warming and Ventilating Co., assisting his father in a series of experiments in the Pantheon, preparatory to the introduction of heating the buildings by means of the "Gurney" stoves. He frequently visited Paris after that time, and was there when the Revolution broke out, followed by the removal of Napoleon III.

Having attended some lectures at the Royal College of Chemistry, he joined as a regular student in 1869, passing the examination in June, 1870, when he obtained a first class certificate and the "Special Certificate" for research work, "On the Action of Normal and Acid Salts upon Ammonium Salts, especially upon Ammonic Chloride," published in the *Journal of the Chemical Society*, 1871, **24**, 785, also in Watt's "Chemical Dictionary," 2nd Suppl., p. 60. In October, 1871, he became private assistant to Dr. Frankland at the Royal College of Chemistry, and was engaged in that capacity

on chemical analyses and research work, one lengthy investigation being for the Russian Government in respect of the destructive distillation of various woods and the possibilities of making use of the gases produced therefrom for illuminating purposes.

He was elected a Fellow of the Chemical Society in December, 1871. In January, 1872, he was appointed chemist to the Bede Metal and Chemical Co., Ltd., Jarrow-on-Tyne. In March, 1873, he received the appointment (following his friend, the writer) as assistant professor of chemistry at the Royal Agricultural College, Cirencester, where he remained until 1878. During his stay at Cirencester he conducted a considerable amount of research work for Professor A. H. Church in animal and vegetable chemistry, on turacin, a bird pigment from the Turaco, containing copper; colein, the colouring matter of the Coleus plant; vegetable albinism; aluminium in plants; eugenol; etc. Being registered as a teacher by the Science and Art Department, South Kensington, he gave a course of lectures at Cirencester in 1874 on inorganic chemistry. In 1878 he was elected a Fellow of the Institute of Chemistry. From 1878 to 1886, Woodcock was associated with the late G. W. Wigner and Messrs. Wigner and Harland, in their practice as analytical and consulting chemists and public analysts.

In 1886 he received an appointment with the American and Continental Sanitas Co., and accompanied the writer to New York, U.S.A., in order to start a factory and branch business in that country, remaining there until March, 1906, when he returned to England and joined the parent Sanitas Co., Ltd., in order to assist the writer in his charge of the chemical and bacteriological laboratories of the company, of which Mr. Woodcock subsequently became a director. During his stay in New York he was largely instrumental in initiating the New York section of the Society of Chemical Industry, and served as honorary treasurer from its formation, a farewell dinner being given to him by the members on March 24th, 1906. He also served as a Vice-President of the Chemists' Club, New York City. Ill-health caused him to resign active work with the "Sanitas" Co., Ltd., in March, 1916, but he remained on the board of directors up to the time of his death.

The research work in which he was engaged with the writer during this latter period of his career was very varied in character, and embraced the results covered by the following joint publications: "Bacteriological Testings of Certain Disinfectants, and the results as Affected by Varying Conditions." (Communicated to the British Pharmaceutical Conference, Cambridge, 1910. *Pharm. J.* 1910, **85**, 157). "The Bacterial Testings of Disinfectants. A Practical Criticism." (*Analyst*, May, 1913.) "The Production of

Formic Acid by the Atmospheric Oxidation of Turpentine." (*J. Soc. Chem. Ind.*, 1910, **29**, 791.) "The Production of Formic and Acetic Acids by the Atmospheric Oxidation of Turpentine." (*J. Soc. Chem. Ind.*, 1912, **31**, 265). "Some Experiments concerning Antiseptic Inhalations." (*J. Clinical Res.*, 1914, October.)

Mr. Woodcock was a member of the Society of Public Analysts, an original member of the Society of Chemical Industry, and served as a vice-president of that body for some years.

The writer first made the acquaintance of his late lamented friend in the rooms of the Chemical Society in the spring of 1872, and enjoyed unbroken friendship down to the time of his decease. Mr. Woodcock, if not a rapid worker in the laboratory, was most exact and painstaking—almost to a degree of fastidiousness—so that his work was always eminently trustworthy. He was of genial character, extremely well read, of the highest rectitude, and his loss will be deeply mourned by all who knew him at all intimately.

C. T. KINGZETT.

PHILIP JOHN WORSLEY.

BORN OCTOBER 29TH, 1834; DIED MARCH 7TH, 1917.

PHILIP JOHN, the son of Philip Worsley, was born in London and lived there during his school and college days. His taste for chemistry showed itself when he was quite young, and was encouraged by his grandfather, John Taylor, F.R.S., and his uncles, who were mining engineers. He entered the Junior School of University College, Gower Street, in September, 1843. In speaking of his school days, he said that he was not successful because he seldom kept his mind continuously on his work; classics did not come easily to him, and he had the greatest difficulty in learning by heart, but he was interested in chemistry However, he worked better when he went to University College in 1850, where he greatly appreciated the teaching of Augustus de Morgan in mathematics and of Thomas Graham in chemistry. He graduated in 1853 with honours in chemistry. Among his fellow-students were George du Maurier, Michael Foster, George Carey Foster, and George Buchanan. The great exhibition of 1851 brought many distinguished scientific foreigners to his grandfather's house in Kensington, which gave the young student of chemistry and prospective mining engineer opportunities of hearing discussion on all the latest discoveries and theories.

In 1853 he went with his uncle, Richard Taylor, on a visit to lead mines at Pontgibaud in the Auvergne, where he was given the run of the works. From Pontgibaud he went by coach to Marseilles, the railway not being opened beyond Lyons; here he

stayed with a great-uncle, Philip Taylor, who had engineering works, which have since become one of the shipbuilding yards of the French Navy—les Forges et Chantiers de la Méditerranée. His next experience was in Germany, where he went to be educated as a mining engineer at the Bergakademie, or Royal School of Mines, at Freiberg in Saxony. On the way he passed through Heidelberg, and was taken by his friend Henry, afterwards Sir Henry, Roscoe to see Bunsen's laboratory. Before attending lectures at the Bergakademie, the students had to take a practical course either in the mines or the smelting works; Worsley chose the latter. On his own initiative he made careful notes of the process accounts, giving the results and cost of the various operations, which were invaluable to him in later days. On his return from Germany in 1854 he took a course of practical chemistry in the Birkbeck Laboratory at University College, London, under Professor Alexander W. Williamson and Assistant Professor Henry Watts, author of the well-known "Dictionary of Chemistry."

In 1855 came his first employment. He was sent to Ireland to assist Dr. Gurlt, a former Freiberg student, in working a new process for extracting copper from poor ores for the Wicklow Copper Co. This only lasted for a month or two, his first regular work being at Rotherhithe, where he started works for Messrs. H. J. Enthoven and Sons for separating silver from lead, superintending the erection of the plant, and constructing subsidiary furnaces from his own plans. While here he joined the Chemical Society, being elected a Fellow on February 4th, 1858. He stayed at Rotherhithe until 1860, when he went to Bristol as assistant manager of the Netham Chemical Works.

In the autumn of 1856 his grandfather, who was treasurer and an original member of the British Association, took him to the meeting at Cheltenham and made him an associate. His friends of the Chemical Society put him upon the committee of Section B of the Chemical Section. It was at this meeting that Sir Henry Bessemer described his process of burning the carbon out of pig-iron, which was the first step towards the modern process of making Bessemer steel. In 1858 Philip J. Worsley and George Carey Foster went together to the meeting at Leeds, where they met the set of young chemists whom he had seen working in Bunsen's laboratory at Heidelberg in 1854. They did not appreciate the social evenings of the Association, but met in each other's rooms and formed what they called Sub-Section B; these meetings were full of fun and interest, and other friends besides the original members asked to be allowed to join them.

In 1860 the Chemical Works at Netham were a small affair with a capital of £15,000. They had been going for a year and a-half,

and were in a very bad way. The new young assistant manager was thrown entirely on his own resources; he knew the theory of the processes, but in practice all was new to him. He soon found that the business was not prospering, and that unless he could improve the manufacture it would soon come to an end. He gradually introduced improved methods and instituted a system of regular sampling and testing the various stages of the work. Common sense with theory as a guide soon began to tell, and the reign of chemical anarchy and muddle gave place to order and system. After three months of probation he was made manager. After a time Netham chemicals got a high repute and were in constantly increasing demand. The plant and capital were increased every few years, and the directors' appreciation of his management was shown by their giving him a place on the board in 1871.

In 1873 he joined with other alkali manufacturers to form the Bleach Association, at which he made the acquaintance of all the leading men of the trade, some of whom were already his friends or schoolfellows. At a later period, when the Netham Chemical Company was merged in the United Alkali Company (1890), he met many of them again and worked with them as a fellow-director, keeping his seat on the board until 1901.

As a young man, Worsley's strong inclination was towards pure science. He imagined that he would always be able to keep up his interest in chemistry, and that he might in his leisure find time to make investigations which would establish him as the equal of the men of science who were his friends. However, instead of working in a private laboratory, he gave his scanty leisure to the cause of education and philanthropy. From the chairmanship of the St. George's School Board (Netham is in the parish of St. George, Bristol) to the vice-chairmanship of the University College, afterwards the University of Bristol, he helped to forward every grade of education in the city. As a Liberal in politics and a Unitarian in religion, he took an active part in public life. His chief recreation in his later years was gardening, and one of his greatest pleasures was the success he obtained in producing new varieties of daffodils by hybridisation.

As a memorial of his great work in connexion with the University of Bristol and his interest in the chemical department, a gift has been made to the chemical library, the interest of which is to be used annually to make additions of books and periodicals. He had given the greater part of his private collection of books on chemistry to the University during his lifetime. A. W.

The Old and the New Mineralogy.

Hugo Müller Lecture, delivered before the Chemical Society on April 18th, 1918.

By Sir Henry Alexander Miers, F.R.S.

When I was honoured by the Council of the Chemical Society with the invitation to deliver the first Hugo Müller Lecture, I was in some doubt whether I ought to accept it. The task it involves is not easy for one who during the last ten years has by administrative duties been taken altogether away from scientific work and who has not been able even to keep in touch with the rapidly increasing literature either in chemistry or in mineralogy.

But when I thought of my old and close friendship with the man in whose memory this lecture has been instituted, and the regard which I feel for his family; when I reflected on the helpful part that he played in strengthening the bond of union between mineralogy and other sciences; and in particular when I remembered the kindly interest with which he encouraged me in my younger days, I felt that the invitation of the Council laid a duty on me which I could scarcely refuse, however ill-qualified I may be to fulfil it adequately.

The excellent obituary notice of Dr. Hugo Müller in the June (1917) number of the Society's Journal sketches in clear outline both the character and the scientific career of this singularly modest and wide-minded man. All who knew him will feel that in him they have lost not only a warm-hearted and sympathetic friend, but also an adviser whose sound judgment and varied knowledge were only equalled by the unselfishness with which he placed them at the disposal of others.

There can, I think, be no more kindly or more useful action than to help young people at the outset of their career to do the work for which they are best fitted by training and inclination; and I am able to speak as one who owed to him, at least to some extent, an introduction to congenial work.

As Professor Armstrong has recorded in the obituary notice to which I have referred, it was largely owing to Dr. Müller's instrumentality, when as President of this Society he was a member of the Executive Committee of the Central Technical College, that the teaching of crystallography was introduced into the Chemical Department of the College.

That was really the first recognition in this country of crystallography as an independent subject, and the first recognition of its

importance to chemical students. I only regret that the recognised position given to crystallography by Professor Armstrong's action has apparently been lost by his retirement.

I was invited by Professor Armstrong to undertake the work, and was thus given the opportunity of teaching a subject in the practice of which I was engaged by my daily occupation as assistant in the Mineral Department of the British Museum.

You will understand, then, that I am glad for this among other reasons to have this opportunity of offering a tribute to Dr. Müller's memory.

Hugo Müller's interest in minerals began in his boyhood, and was no doubt stimulated during his student days at Leipzig by the influence of Professor C. F. Naumann, whose lectures he attended. Indeed, Professor Armstrong tells us that his first intention was to devote himself to geology; and although in later life his professional energies became more and more absorbed by chemistry and its applications to the industry with which he was concerned, and his leisure hours by botany and gardening, yet he always maintained his interest in minerals and mineralogy, and his acquaintance with the literature of the subject. Indeed, from 1901 to 1904 he was President of the Mineralogical Society.

He was always a great admirer of fine mineral specimens, and left behind him a very complete and representative collection which has been presented by his widow and daughter to my old department in the University of Oxford.

It may seem singular that with so pronounced an affection for minerals Müller was much more concerned to devote his analytical skill to vegetable than to mineral products. When he retired from business he carried on researches into the chemical constitution of organic products, mostly of vegetable origin, and did not, as might have been expected, take up work on the minerals, in which he was so deeply interested. In fact, his published mineralogical work was actually confined to the early years between 1850 and 1860.

Whether he ever intended to do scientific work on his mineral collection I am unable to say; but had he done so on his retirement from business, it would have been in very different circumstances from those which prevailed fifty years earlier, especially as regards the attitude of mineralogists towards chemistry.

It has occurred to me that I may make the present occasion an opportunity for contrasting this attitude as it was in 1850 with what it was at the beginning of the twentieth century when Müller retired from business, and what it is at the present day.

The period of his student days in Leipzig seems to me to have been a very interesting and a very critical period in the history

of this science, which was then just beginning to recover from a dangerous disease.

To explain what I mean, let me recall the views which were held by many of the most influential mineralogists at, or shortly before, that date.

In the mineralogical world, full sway was then still exercised by the "natural (or natural history) system" of Werner, of Freiberg, which had been developed and elaborated by his successor Mohs.

According to this system, and here I am quoting the words of Mohs himself, "Mineralogy is the natural history of minerals," and "the natural-historical properties are those with which Nature has endowed the bodies which it produces, provided those properties as well as the bodies themselves remain unaltered during the examination." The only characters of minerals, according to this view, which are of fundamental importance, and which are therefore to be used for the purpose of discriminating between species and of classifying them, are the external or natural-history properties, such as specific gravity, lustre, hardness, colour, frangibility, and crystalline form. Clearly this definition entirely excludes the chemical properties. To quote again the actual words of Mohs: "Properties which can only be used during or after a change cannot be employed agreeably to the principles of Natural History and must therefore be excluded from mineralogy. Properties of this kind are the fusibility of minerals examined before the blowpipe; their solubility in acids; phosphorescence produced by heat; chemical analysis instituted to ascertain the quality or relative quantity of the component parts." "If a person intends to acquire solid information in mineralogy he should examine well-arranged collections."

These views served, no doubt, to stimulate collectors of minerals and directed a good deal of attention to the desirability of bringing together the best possible specimens, and of comparing the external characters so as to discover their relationships. But that the chemical properties should be completely ignored on principle seems now almost incredible, especially when we remember that Berzelius had already published in 1816 a chemical classification of minerals and had even claimed that mineralogy is really only a branch of chemistry. The authority of Berzelius was even greater than that of Werner or Mohs; yet their methods persisted for another generation at Freiburg, which, as a great mining centre, was also a great centre of instruction in mineralogy.

It was during Müller's student days that the revolt against their ideas took place.

To obtain a general survey of the successive changes in the history of the science, one cannot do better than refer to the successive editions of J. D. Dana's "System of Mineralogy," which first appeared in 1837, and of which the sixth edition (1892) was prepared by his son and successor, E. S. Dana. In the first and second editions Dana not only adopted the natural history system then in vogue, but even endeavoured to make it more precise by a Latin nomenclature; but in the third edition, published in 1850, he suddenly shook off the trammels of this system and adopted a chemical classification.

Nothing could better illustrate the change which came over the science in the middle of the nineteenth century than the preface to this edition. In it the author says: "The Science of Mineralogy has made rapid progress in the past six years; chemistry has opened to us a better knowledge of the nature and relation of compounds; and philosophy has thrown a new light upon the principles of classification. To change is always seeming fickleness. But not to change with the advance of Science is worse; it is persistence in error; and, therefore, notwithstanding the former adoption of what has been called the Natural History System, and the pledge to its support given by the author in supplying it with a Latin nomenclature, the whole system, its classes, orders, genera, and Latin names have been rejected. . . . The system has subserved its purpose in giving precision to the science and displaying many of the natural groupings which chemistry was slow to recognise. But there are errors in its very foundations which make it false to nature in its most essential points; and, in view of the character of these errors, we are willing it should be considered a relic of the past."

The year in which these words were written was the very year in which young Hugo Müller entered the University of Leipzig.

It must have required no small courage for a man in Dana's position to make such a recantation, but the benefit to the science was great. His "System" was becoming the standard book of reference for systematists. His rearrangement of species and adoption of a classification based on chemical constitution carried much weight.

It is not surprising that Hugo Müller as a student became interested in a science which was just at that time the focus of a discussion involving such fundamental issues, a science which in spite of its antiquity and importance had for thirty years, in Germany at least, endeavoured to close its doors against the chemist. It is fortunate that there were a few men like C. F. Rammelsberg and Gustav Rose who perceived the vital import-

ance of chemical composition in the study of minerals and exercised sufficient influence to counteract the dangerous authority of Mohs. Rammelsberg in 1847 published a volume of translations of the works of Berzelius bearing on the classification of minerals, and was devoting himself to their systematic analysis. I have already in a memorial lecture sufficiently described to this Society his contributions to the subject. It was his analytical work which really rendered possible a scientific classification. Gustav Rose in 1852 published his crystallo-chemical mineral system, which has served as the basis of all scientific classifications of minerals since that date. In the preface to that work he says: "It might appear that I have adopted a mixed principle in constructing this system: but this is not the case. For though I fully agree with the view of Berzelius that the system should only have regard to the nature of the elements combined, and the formulæ which express the composition, yet it must be borne in mind that the crystalline form is merely the expression of a definite composition, and in this way it is all the more certain a guide because in many, perhaps most, minerals we are still far from such a complete knowledge of the composition as is required by Nordenskiöld's system. The crystalline form tells us much more than the mere chemical formula; it tells us how the atoms are united, and this difference in the mode of union of the atoms often conditions the external differences of bodies even more than the actual differences between the atoms."

Dana, even when he originally adopted the natural system in preference to the chemical system, had expressed the hope that in time the two would prove to be identical: but the principle of isomorphism which was destined to effect this reconciliation seemed at that time to be only an obstacle.

For example, Whewell, in an essay on the classification of minerals, published in 1828, had pointed out how desirable it would be if some coincidence could be found in the chemical and mineralogical systems; but he argued that the then recently discovered property of isomorphism rendered a chemical classification impossible, since a mineral may be from the chemical point of view a mixture of an indefinite number of species.

In his "History of the Inductive Sciences," thirty years later, he still despairs of the attempts to reconcile the two systems, and says: "The combination of chemical, crystallographical, physical, and optical properties into some lofty generalisation is probably a triumph reserved for future and distant years."

The conflict between the two systems was to some extent prolonged by the fact that, even though the purely chemical system might be scientifically correct, it did not afford the means of prac-

tically distinguishing between mineral species except by long and elaborate analyses, and even these might fail, since different minerals may have what is apparently the same percentage composition; on the other hand, the external characters did enable the well-trained mineralogist to determine a species with rapidity and precision. It was perhaps natural, therefore, that Freiberg, the centre of training for miners and practical mineralogists, should espouse the system of Werner and Mohs.

Naumann, who had been professor at Freiberg before he came to Leipzig, may have been predisposed in favour of it, but he did himself adopt a system based on the chemical characters; for, as he said, "they represent the actual material, the substratum which is the basis of all morphological and physical phenomena, and which finds its scientific expression in the chemical formula." But he was even more of a crystallographer than a chemist, and emphasised the equal necessity of taking form as well as composition into account. His text-book, "Elements of Mineralogy," ran through five editions between 1846 and 1859, and exercised a far-reaching influence. In the later editions, his system was practically identical with that of Rose.

I have dwelt at some length on the controversy between the adherents of the two systems of classification, not only because it was a controversy which divided mineralogists into two schools of thought, even up to the time when Müller went to Leipzig, but also because a very important principle was at stake and because little is said about this in the histories of chemistry where the controversy is mentioned. It was not merely an academic question of classification or one of practical utility, neither was it a matter which only concerned mineralogists. It was really a question of mental attitude towards scientific problems.

At the beginning of the century there had been a somewhat similar struggle concerning the relative importance of chemistry and crystallography for mineralogists. This resulted from the great advances in crystallography made by the Abbé Haüy following on the great advances in chemistry made by Berzelius. But at that time there was no reaction of the sort represented later by Mohs and his school. Even Werner himself was not prejudiced like his successors. He attached the greatest importance to chemical composition in a system of classification, whatever exaggerated views he may have held concerning the value of external characters for the practical determination of mineral species.

The contrast between the attitude of Mohs and that of Haüy is evident to anyone who reads the introductions to their respective treatises on mineralogy.

In his zeal to confine the science within what he considered its proper bounds, Mohs endeavoured to dissociate it not only from chemistry, but from geology. "Natural History," he says, "considers the natural products as they are and not how they have been formed." And again: "It is a matter of the highest importance to keep the sciences perfectly distinct from each other and strictly within their respective limits."

Haüy, on the other hand, had recognised to the full the value of co-operation between all the sciences concerned, including not only chemistry, but also physics and geology.

The contention of Mohs and his school that it was unnecessary, or even improper, to apply chemistry to the study of minerals, seems to me to represent the most dangerous mental attitude which is possible for a scientific man.

We are apt to regret the growing specialisation in science, and to think that half a century ago it was almost impossible for a scientific worker to be much of a specialist. But surely the school of Mohs was guilty of the worst type of specialisation. The earlier workers in general were no narrow specialists, because the dividing lines between the sciencs were not decisively laid down. To Haüy, or Mitscherlich, to Wollaston, Brewster, or Rose, each discovery was a new scientific problem, and they were not much concerned to decide whether to use the methods of physics or chemistry or geology for its solution.

Frontiers have always been the scenes of greatest activity, and it is precisely on the borderland between two sciences that the most fruitful progress has been made.

A man is not a specialist to the detriment of himself or his science, even though he devotes his whole life to the study of a single problem, provided that he makes sufficient excursions over the frontier in the interests of his life's work. But Mohs and his school endeavoured to isolate mineralogy (including crystallography), and to make it an independent science apart from chemistry, physics, and geology, instead of regarding it as a meeting ground of these sciences. The aloofness engendered by their action did great harm both to mineralogy and to chemistry; it tended to withdraw mineralogy and crystallography from the purview of chemistry, and it also closed the eyes of mineralogists to advances in chemistry that should have been of vital importance to them.

History repeats itself, and what has happened before may happen again. This lectureship will, I hope, always be one of the safeguards against exclusiveness and specialisation and will aid mineralogists and chemists to understand and help each other. If

it does this, it will perpetuate the spirit of the man whose name it bears.

The harm of this isolation extends to matters that appear to concern only systematic mineralogy, such as classification. After all, a classification which is right or wrong for minerals must be also right or wrong for other crystallised substances if it is based on what is essential; its merits or shortcomings would sooner or later be disclosed if the underlying principles were applied to other substances.

One regrettable result of the policy of isolation was that for a long period the study of minerals was divorced from that of organic or even of other inorganic substances, and that the study of crystallography was confined to mineralogists. This was partly, no doubt, due to the fact that minerals afford such splendid examples of crystallisation, and partly because a knowledge of the crystal properties is so useful in their practical identification.

Let me here finish with this subject of classifications and remind you that it was not until a later period that attempts were made to include all crystallised substances in a wider scientific survey and in a common study. Indeed, it is only within the last few years that a comprehensive catalogue of them all has been attempted by Groth in his "Chemical Crystallography," which began to appear in 1896, and is not yet completed.

During the same period, the Russian crystallographer Fedorov has been constructing a general table of crystalline substances so arranged that it is possible to identify any known substance by means of the characteristic angle of a single crystal when once it has been set up in the right position according to the rules which he has formulated. Mr. Barker has recently shown in a striking example the practical utility of this table even for the purposes of the medical man, by thus identifying a minute crystal of salol of intestinal origin (*Lancet*, May 26th, 1917).

That there should be several classifications made for different purposes within the same science is probably a quite wholesome principle: one may, for example, bring out constitutional relationships, and another be useful for determinative purposes.

But of far greater scientific importance than the systematic classification of minerals or the discovery of new methods for their identification is the question, What are the actual relations between the physical, geometrical, and chemical characters of a crystallised mineral? Only in proportion as this study has grown by co-operation with chemistry and physics did the science of mineralogy advance successfully along the path opened up by Haüy and

Berzelius, by Mitscherlich and Wollaston, by Rose and Rammelsberg.

In this new purpose, and in the changed attitude of mind that it involved, lies, I think, the essential difference between the old and the new mineralogy which it is the object of this address to emphasise, and it is time for me to turn to the later developments.

The newer mineralogy with this purpose in view has only made progress by the employment of every available physical and chemical method in the accurate study of carefully selected specimens.

In the first instance, it was difficult to do much with isolated species for lack of suitable experimental methods, such as have been developed during the present century. Having ascertained the exact chemical constitution, to determine with any reasonable probability the actual arrangement of the atoms or molecules in a crystal which may account for its form and physical characters was too difficult a problem with the experimental resources then available.

But the relations between different minerals belonging to the same group in which it could be assumed that, whatever they may actually be, the structures and constitution are similar, were gradually worked out.

The laws of vicarious replacement of one element or radicle by another were studied, and the variations of physical characters with the change of chemical composition in many an isomorphous series constituting a mineral group were successfully traced; and it must be confessed that for these researches the foundations had not infrequently been laid by the adherents of the natural history methods, for they had recognised many minerals as belonging to very definite mineral species and groups in spite of their chemical differences.

It was understood, for instance, that the pyroxenes or the felspars, whatever might be their percentage composition, do constitute a group, and it was natural to conclude that the remarkable similarity in physical properties shown by the various members of the group must correspond to a mutual replacement of certain elements or radicles, though the exact nature of these radicles might be still doubtful. For example, the growing importance of petrography and the use of the polarising microscope led to a vast amount of study being devoted to such minerals as the felspars, so that it was not long before it became possible to determine with accuracy by means of the microscope the exact chemical constitution of a minute crystal grain belonging to this group without analysis.

On the other hand, it is still doubtful how the elements are actually associated with each other in the mineral, or what radicles are to be regarded as corresponding with each other in such isomorphous groups, mixtures, or solid solutions. To establish this sort of knowledge, a great deal of very careful chemical analysis was necessary, accompanied by an equally careful physical study of the specimens analysed. It was to work of this character that most of the important advances in chemical mineralogy during the second half of the nineteenth century are due.

I select as a conspicuous example of this type of research Penfield's investigation of topaz, to which a very definite chemical formula had been assigned, although it was known that the mineral exhibits some variations both in composition and in physical characters.

The most reasonable view seemed to be that the radicle Al0 may be replaceable by the radicle AlF_2. The insignificant and variable traces of water were ignored. Careful analyses and accurate measurement of the angle between the optic axes, however, led Penfield to the conclusion that the optical characters vary regularly with the proportion of water, or rather of hydroxyl, and that the simple formula $Al_2F_2SiO_4$ is entirely satisfactory if it be understood that fluorine is replaceable by hydroxyl.

Many minerals and mineral groups have now been investigated with equal success: but almost every mineral contains an intermixture of various allied compounds as well as enclosures of other minerals, and therefore it is rather to the study of pure laboratory products that we have to look in the first instance for more precise knowledge concerning the relations between form, physical properties, and composition.

A vast number of isomorphous groups have now been studied in detail and with accuracy.

Tutton's classic investigation of the sulphates and selenates of potassium, rubidium, cæsium, and ammonium is one of the most conspicuous and complete examples. Others extending over the whole field of inorganic and organic compounds are recorded and discussed in Groth's "Chemical Crystallography."

I need only mention such studies as those of Jaeger on the benzene derivatives and the nitroanilines, of le Bel and Ries on the platinichlorides, of Jee, Rodd, Colegate, and others working with Armstrong on the benzene derivatives, and the investigations associated with the names of Gossner, Steinmetz, and others working with Groth at Munich.

All these advances in chemical crystallography have only been rendered possible by a vast amount of research on countless sub-

stances examined in the laboratory by a new generation of chemists who had acquired a knowledge of the methods of crystallography and an interest in its principles.

Although in these and similar investigations the exact morphological effects of the replacement of one element or radicle by another have been determined, I fear it cannot be claimed that the general laws of morphotropic action have been discovered even at the present day.

Now let me return for a moment to the year 1850. That year which, as I have indicated, was notable in the history of systematic mineralogy, was even more important in the history of crystallography, for it witnessed the publication of Bravais's memoir on the regular arrangement of points. This research first established a principle capable of explaining the homogeneity of crystals, their symmetry, the distribution of their faces, and their cleavage.

The mathematical treatment founded by him was elaborated by Sohncke and others, until finally and independently, towards the close of the nineteenth century, Schönflies, Fedorov, and Barlow determined and tabulated all the possible arrangements of material which can build up a homogeneous crystal, and so completed the pure geometry of the subject.

But when it came to the application of these geometrical principles to actual crystals and to the question what are the units which are arranged in this manner, it was the custom to fall back upon the assumption that these are "physical molecules" consisting of an unknown aggregate of "chemical molecules." Indeed, an attempt made by Sterry Hunt in 1891 to determine the degree of polymerisation from the specific gravity, hardness, and solubility led him to the conclusion that there are 584 chemical molecules in the physical molecule of calcite and 950 in that of quartz.

When speculation runs riot, it is a sign that experiment is needed. It is clear that there was need of new experimental methods to curb such wild views, and not only in this, but in other branches of mineralogy; for there were equally uncontrolled speculations concerning the origin of minerals, and especially rocks, and the processes by which they have solidified from solution or fusion.

It is in these later experimental methods that what I venture to call the new mineralogy distinguishes itself from the old mineralogy belonging to Müller's student days. And the change has mainly been rendered possible by recent advances in physics and chemistry, and particularly in physical chemistry.

There are two stages in the history of a crystallised mineral, that which terminates immediately before it solidifies and that

which begins at the moment of solidification. Both are of equal importance and interest to the mineralogist, and upon both a flood of new light has been thrown by recent investigation.

The excellent abstracts of the *Journal* of this Society and its "Annual Reports on the Progress of Chemistry" record all the important researches bearing on these problems. I need not do more, therefore, than select one or two conspicuous examples.

To deal first with the origin of minerals and the stages that preceded their crystallisation.

The application of the laws of physical chemistry, especially the recently discovered properties of solutions, found its most fruitful results in the studies of the Stassfurt deposits by van't Hoff and his pupils. There can be little doubt that we have now a well-established history of the manner in which these deposits have been laid down from solution and the nature of the solutions from which they have crystallised. Before these researches, there had been much speculation as to how such deposits might have originated from the evaporation of saline water, but it was only by the laboratory experiments begun by van't Hoff in 1897 and carried on through a series of years that the geological history of the deposits has been finally and fully reconstructed, including the order and conditions of deposit of more than thirty mineral species.

Nothing like this had previously been achieved. The processes previously invoked in explanation of the origin of minerals had been largely hypothetical, not experimental; with these researches, a new chapter in the history of mineralogy was opened.

It is unnecessary to refer to any details of the experiments. The excellent summary published by Dr. E. F. Armstrong in the British Association Report for 1901, and since that date the Annual Reports of this Society, have helped to make them widely known.

To take another example. It is of vital importance to the geologist that the history of rock formation should be deciphered, and for this purpose the newly established laws of physical chemistry were also directed to the problem of the crystallisation of the silicates.

Igneous rocks were for the first time regarded as solutions, and the physical properties of solutions were applied to the crystallisation of rocks from molten magmas. Vogt, in particular, endeavoured to show by his researches on slags, and with remarkable success, that they have crystallised in accordance with the laws of eutectic mixtures and of mixed crystals. A whole new field of research was thus opened up; but here again much of it was highly speculative until within the last few years the actual crystallisation of molten silicates has been brought within the range

of experimental study. Doelter, of Graz, and his pupils are responsible for much of this work, but more recently the experiments conducted at the Geophysical Laboratory at Washington have constituted a very remarkable advance.

The appeal to experiment has replaced a mass of speculations concerning theoretical solvents and the order of crystallisation, which were based only on field observations and bulk analyses. Now that sufficiently high temperatures can be attained, these investigations are of the greatest importance both to the geologist and to the mineralogist, since they reproduce in all probability the main conditions under which rocks have crystallised. One feels that for the first time the laws of their solidification are being traced and that they can be verified by experiment.

I need not do more than quote as examples the very full researches by Bowen and Anderson on the binary system magnesia and silica, and the ternary systems diopside–forsterite–silica and anorthite–forsterite–silica, and more recently by Bowen's investigations on diopside–albite–anorthite, and those by Rankine and Wright on the system lime–alumina–silica.

Such questions as the order of crystallisation and the actual position of eutectic mixtures in the process of solidification can now be determined by actual experiment, and not merely by the microscopical study of the solid rock. Not the least remarkable result of many of these experiments is the absence of the eutectic structure so characteristic of alloys, suggesting that perhaps too much importance may have been attributed to it by petrologists.

Some of this work has also thrown valuable light on the past history of rocks and minerals.

To quote only one example; direct experiments on the melting and inversion temperature of quartz have indicated that at 575°, within a very close approximation, it suffers enantiotropic change to the phase now recognised as β-quartz, and that above 800° quartz is no longer stable at ordinary temperatures, but becomes converted into tridymite. It is therefore suggested that quartz may be used as a geological thermometer serving to record the maximum temperature which has been reached by certain rocks. A similar use may perhaps be made of other minerals.

Such work as that of Bowen on the melting points of the felspars and their mixtures is of the highest value in tracing the past history of rocks and their minerals. His conclusion that albite and anorthite have the same molecular complexity in the liquid as in the solid state is one more stage in the simplification of our ideas concerning the constitution of minerals.

The pressure is, of course, an all-important factor which must

not be left out of account in speculations concerning the past history of rocks. Change of pressure may affect the order of crystallisation of the minerals which separate, and may determine their nature, as profoundly as change of temperature. Experiments at high temperatures combined with high pressure are now for the first time becoming possible with improved laboratory apparatus.

These experimental researches on the application of the law of solutions to minerals are not confined to silica and the silicates, but have already been extended at the geophysical laboratory to the copper sulphides and the oxides of iron. Experiment has yet to be applied successfully to such questions as magmatic differentiation, the effect of mineralising agents, pneumatolysis, and many similar problems. On the more vexed questions relating to the history of vein minerals and the large class of secondary deposits which line the cavities and fissures of the earth's crust, experiment will have much to say, though it may be a long time before experimental investigation on these subjects can be fully developed.

In the work of van't Hoff and in that of the Washington geophysicists, we have two conspicuous examples of what I mean by the new mineralogy as applied to the problem of the origin of minerals and rocks, that is, to the stage through which they pass up to the moment of solidification.

This application of experimental methods in which an attempt is made to realise the conditions of mineral growth replaces a vast amount of speculation with which the science was burdened during the last fifty years, and it unsettles some of the elaborate classifications, especially of rocks, which have occupied too much time and thought during the same period.

Surely classification as a means of arriving at general laws is an unsafe guide in the inorganic world if based to any large extent on hypotheses; it only serves to perpetuate them. Its proper function is to record the application of the general laws established by experiment, and any classification must inevitably change with new experimental results. For this reason, the attempts which are now being made by a group of American geologists to establish a natural classification of rocks with a new nomenclature are surely doomed to share the fate which befell the natural classification of minerals.

Let us turn next to those problems that concern the nature of minerals after they have solidified.

In this field also there had been an immense amount of speculation during the last half of the nineteenth century concerning the nature and arrangement of the units which constitute a crystal.

Somewhat surer ground was reached by the conception of topic axes introduced by Becke, and employed by Muthmann and Tutton, which gave suggestive evidence concerning the relative dispositions of the crystalline units along corresponding directions in a series of isomorphous substances, and indicated the increased or diminished separation of these units along a given direction when one element or radicle is replaced by another.

The importance of the molecular volume in these relations has been emphasised by Barker's experiments on the parallel growth of one substance on another; I have considerable faith in this as a sure experimental method which has yet to be used in tracing similarities of structure even where there is no chemical relationship.

The crystallographic study of closely allied substances has further led directly to speculations concerning the relative positions of the *atoms* in the crystal structure, as, for example, in Muthmann's study of the perchlorates and permanganates, which was the first conducted from the point of view of topic axes; and, again, the relationships between the nitrates and carbonates led early to similar speculations concerning sodium nitrate and calcite.

To take another example in which this problem was attacked in a different way, Sollas endeavoured to ascertain the positions of the elements in sodium nitrate by comparing the specific refractive energy of the crystal in its two principal directions, and in the case of potassium copper chloride he combined this feature with the dichroism which he interpreted as indicating that the crystal is of a cuprous nature in one direction and of a cupric nature in another.

It is interesting to note that such speculations were already assuming that in most crystals the structural unit is probably an aggregate of not more than a few molecules, and in some perhaps the molecule itself. This was a great contrast to the earlier assumptions concerning polymerisation in the crystal molecule. Indeed, it was not long before expression was given to the extreme view that the structure is to be regarded as a regular arrangement of atoms in which the grouping into molecules is merely a geometrical fiction, whatever may have been their significance immediately before the act of crystallisation. This view was stated in a paper read by Professor Groth to the British Association as far back as 1904, in which, speaking of new ideas concerning crystal structure, he said, "it is unnecessary to assume the operation of any 'molecular forces' in addition to the forces which act upon the atoms themselves."

If, as I have said before, we are not yet in sight of the general

laws of morphotropic action even within groups of closely allied substances, we are still further from the supreme problem how from the chemical composition of a substance to deduce the form and physical properties of its crystal. The great test of a theory is the question whether it will enable us to predict, and in this sense there is as yet no satisfactory theory of the nature of a crystal. A bold and original attempt has been made by Pope and Barlow with some measure of success, and their theory of crystal structure which is based on the atom as the structural unit and endeavours to explain the form of the crystal from the atomic magnitudes, as indicated by the valencies, combined with the principle of close packing, has already inspired several very important investigations.

But in regard to the structure of the solid crystal, just as much as for the process of crystallisation to which I have already alluded, the need was for new experimental evidence—for some method of investigation which could explore the structure with a finer discrimination than that provided by the transmission of light or heat.

And now, as all the world knows, it seems that direct evidence concerning the arrangement of the parts of a crystal, the magnitude of the intervals between them, and even the spacing of the atoms, is supplied by *X*-ray methods, and in particular by the classic investigations of the Braggs.

In the history of crystallographic discoveries it has not infrequently happened that the crystal has first revealed some unknown physical phenomenon, has then supplied the mechanism or the material for studying it, and for establishing the principles by which it is governed; then, finally, these principles have been turned back upon the crystal in order to explain its nature. This was so with the phenomena of double refraction; calcite disclosed the new fact of double refraction to Bartholinus and Huygens, and this led to the discovery of the laws of propagation of light; these in turn were applied to the study of crystals, and have proved the most potent instrument that we possessed until lately for researches into crystalline structure. It was so again with circular polarisation and with pyroelectricity.

And so it is now with the new *X*-ray methods. The crystal reveals the new facts and then lays itself bare to attack from the physical weapon which it has forged. Indeed, in these remarkable investigations it is difficult to say which is the more valuable, the evidence which the crystal gives concerning the nature of the radiations or the evidence which the radiations give concerning the molecular or atomic intervals in the structure of the crystal.

If I do not dwell at length on these researches, it is not through any failure to recognise them as by far the most important advance of recent years, even in the science of mineralogy, but only because they are now so familiar to the scientific world. They have, of course, not destroyed anything that had been established by mathematical deduction from previous experimental evidence, but they have supplied new experimental methods of a most fundamental character for the study of crystals.

The assumption on which Bragg's interpretation is based, namely, that the crystal consists of material distributed in equally spaced plane layers or in layers separated by intervals which recur regularly, corresponds with all that had been laid down by purely geometrical considerations, and it has been confirmed by all that we know about the physical properties of crystals.

Indeed, if it were needed, evidence of the existence of plane internal layers parallel to possible faces of the crystal is supplied by the *X*-ray analysis. For Canac and others have shown that it is possible to measure the angles of a crystal by *X*-ray reflections from the internal planes just as certainly and almost as accurately as by the reflection of light from the external faces of the crystal.

The care which must be exercised in the interpretation of *X*-ray measurements in their present early development is illustrated by Vegard's observations on the rutile group of minerals, in which a structure based on the reflections observed by him has been subsequently shown to be erroneous, because certain intermediate reflections were overlooked.

Whether the *X*-ray analysis can supply evidence as to the existence or nature of the chemical molecule in the crystal is a more difficult question into which I do not feel competent to enter.

In crystallographic research I have nothing to record quite corresponding with the work of the Washington geophysicists, for the simple reason that there is for crystallography no department corresponding with the geophysical laboratory.

In my opinion, the importance of the study of crystals has now become so great, not only for the identification of substances by crystal measurement, but also on account of the new knowledge which modern crystal study is contributing to problems belonging to different sciences, that there is real need for a department of pure crystallographic research, one in which such studies can be carried out quite independently of elementary teaching or of immediate applications, and without being tied to mineralogy. I venture to hope that it will not be long before some such department is founded either in connexion with one of our universities or elsewhere.

There is yet another notable field of work in which the later physical discoveries have opened up new experimental methods in mineralogy. The past history of minerals may now be discussed in the light of their radioactivity, and the study of radioactive changes is giving some indication of a process of progressive change, if not in the minerals themselves at least in the elements which they contain. For the first time, therefore, speculations concerning the age of certain minerals can be based on direct experimental evidence.

The remarkable pleochroic haloes which surround zircon and other radioactive minerals enclosed as microscopic crystals in mica, cordierite, and other rock-forming minerals, were investigated by Joly from this point of view; and in the hands of Strutt, Boltwood, and others the proportions of uranium, radium, thorium, helium, and lead in radioactive minerals have been made an instrument not only for exploring the history of the disintegration changes in these elements, but for estimating the actual age of the minerals. A new importance now attaches to the accurate analysis of such minerals in respect of rare elements which previously escaped notice, and also to the choice of the specimens analysed, for, as Boltwood points out, it is necessary to distinguish between the more ancient primary minerals and those of secondary, and therefore of more recent, origin.

From the mineralogist's point of view, we have passed out of the stage in which the object is to ascertain the formula and to study the mutual replacements of elements and radicles in order to classify minerals into definite species, and have begun to study the mode of association of the elements and radicles within the mineral, both now and during its past history.

In selecting only three or four conspicuous examples of the progress of mineral chemistry during the last fifty years, I have, of course, passed by without notice many very remarkable advances made in other branches of the subject, such as analytical methods and interpretation of analyses, the synthesis of individual minerals, the alterations, replacements, and transformation of minerals both in nature and in the laboratory, the improvements in apparatus for the accurate measurement of physical constants, new methods of separation, the introduction of microchemical analysis, the relations between colour and radioactivity, and a host of other advances.

I have also omitted specific mention of all the recent work on the constitution of the natural silicates, and this for a reason which I must state.

The history of modern views concerning this, the most important

group of minerals (constituting with silica about 90 per cent. of the earth's crust), begins, not long after the period to which I have confined my survey, in 1864 with Tschermak's discovery of the nature of the felspar group as mixtures of albite and anorthite. This led the way to attempts to explain the analyses of many other complicated silicates as mixtures of compounds not so similar to one another as those which had previously been classed as isomorphous, and in some instances far more dissimilar than albite and anorthite.

When, however, such minerals as the pyroxenes, amphiboles, mica, and tourmaline were discussed, the analyses could only be interpreted on this principle by the aid of a host of possible silicates which are not known to exist; and although some experimental guidance in these speculations has been supplied by the work of Tschermak, Schneider, Thugutt, and others on the acids which could be isolated or the residues which could be obtained by decomposition of the mineral, yet the interpretation of the analyses remained to a large extent hypothetical.

The evidence supplied by pseudomorphs, which show the initial and final products in the case of an altered mineral, cannot give any sure information about the solvents which have acted or the intermediate minerals which may have been produced during the process of change. Even experiments on the decomposition of silicates only in general produce compounds which are stable, and lose sight of compounds, unstable in themselves, which may enter into the constitution of the mineral. In the pyroxene group, for instance, synthetical experiments indicate that the diopside molecule may form a solid solution with several unstable silicates, as well as with alumina or ferric oxide, so that Rammelsberg's view of the group as a mixture of the diopside molecule with alumina is not necessarily more unreasonable than Tschermak's more usually accepted interpretation founded on the analogy of the felspars.

And if we make a general survey of the views which have been expressed on the constitution of the silicates, and especially of the alumosilicates, including Vernadsky's theory of the chlorite nucleus and the mica nucleus, and the more recent and attractive hexite–pentite theory of W. and D. Asch, we have to confess that we are still waiting for more experimental evidence before we can be on sure ground. In so far as these theories suggest new experiments, they perform a most valuable function, but they are not to be regarded as in any way equivalent to experimental results.

Synthetical work such as that of Clarke, Lemberg, and Doelter; the discrimination of solid solutions from double salts by careful melting-point determinations; study of the properties of pure

artificial silicates, their combinations and disintegrations; the manufacture of additive compounds and derivatives; the study of such replacements as those of water by alcohol, benzene, and other substances in the zeolites investigated by Friedel, and the adsorption experiments of Grandjean—these are examples of the sort of researches which must be largely extended before constitutional or structural formulæ can be assigned with any confidence to the silicates, and especially to the alumosilicates.

For the present, the freedom of speculation which is possible concerning the chemical structure of minerals bears some resemblance to the unchecked freedom with which the physical and geometrical structures were handled before the advent of *X*-ray methods and the unrestrained speculations on the crystallisation of magmas and mineral solutions which prevailed before the experimental methods of physical chemistry were applied. We still await the key of experiment which may unlock the secret of the chemical constitution of the silicon compounds.

For this reason, without desiring to ignore their interest and importance, I pass over the whole subject of modern theories concerning the chemical structure of the silicates.

Let me, finally, ask the question: In what fundamental respects does the new mineralogy differ from the old of fifty years ago, and what are the prospects for the future? Is it anything more than the pursuit by new methods of the old problems? A more refined study than was possible then of the characters and properties of minerals? And the answer, I think, is that it is a great deal more than this, for the whole purpose of the quest has changed. Our object is no longer merely to trace the relations between different minerals, neither is it our purpose to classify them as animals and plants are classified in order to ascertain the laws that govern these relations. The importance of such classification and study of characters in the biological sciences is due to the fact that the record is one of constant change and development: the careful definition and study of species leads to the laws of evolution. In the mineral kingdom there is apparently no such prospect. Our main purpose is now not to discover how one mineral has been evolved from another, for there is no such evolution, or even how it is related to others, but how it has been constructed from its constituents. We are concerned with the question how its elements came together, and how they are united to form the mineral; and why among the elements that build up the earth's crust only certain combinations occur as minerals, whereas millions of combinations are theoretically possible. The wonder is not that there are so many minerals, but that there are so few; that mineral

species, for example, are so vastly outnumbered by the species of insects.

So long as the crystal unit was supposed to be an unknown multiple of the chemical molecule, these problems seemed far from solution, but now that we appear to be better justified in dealing, not so much with the arrangement of molecules as with the arrangement of atoms in the crystalline structure, one cannot help feeling that the structure must be one of greater simplicity than the complicated silicate formulæ seem to indicate. We may surely hope that minerals will prove to be comparatively simple groupings of the elements, that the discovery of the laws which determine the limited number of minerals existing as stable substances will lead us to a clarified vision of the conditions which determine equilibrium in non-living matter on the earth's surface, and that we may expect an answer to the question why the elements have come together and how they are united to form the beautiful compounds which constitute the mineral kingdom.

This change in the scientific prospects of mineralogy is due to the advent of new experimental methods and principles. The promise of a revived interest and an increased progress in this science lies in the application to minerals of every new experimental treatment, physical or chemical, that can be employed.

In this, as in many other sciences, far too much energy has been expended in the past on the repetition and refinement of old investigations, on the mere improvement of old methods of research or of apparatus, on questions of nomenclature or description. Although I do not wish to underestimate the value of accurate data patiently accumulated by prolonged and careful research, without which no sound foundations can be laid, yet I feel that for long periods mineralogy stagnated because time and energy were occupied in compiling interminable lists of uncertain crystal faces or in the analysis of impure specimens.

The real advance takes place when new methods of attack are turned upon the old subjects.

The physical properties of solutions, X-ray analysis, and radioactive changes are the three examples which I have quoted; they have infused new life into the science; but they are only three, and will have to be multiplied indefinitely.

Minerals deserve all the study that they can get; they supply the most perfect and the most varied materials; almost every known element is contained in them; they are extraordinarily stable compounds; they teem with problems, owing to the variety of conditions under which they exist or have been formed.

Especially would I attach importance to the fact, too often for-

gotten, that mineralogy is one of the natural history sciences, and therefore deals with natural objects not only as we find them in museums, but investigates their relations and their past history; while it studies their properties by applying to them all the known resources of the laboratory, it also studies through them the operation of the laws of nature, both now and in the distant ages of the past. In mineralogy, as in botany and zoology, it is in general impossible to reproduce past conditions; they have gone for ever. But there is this great difference between mineralogy and the biological sciences. Whilst they trace the history of changing species in the light of modern experiments and observations, the only record of their past, and that a secondary and an imperfect one, is supplied by fossils: the organisms themselves have disappeared.

On the other hand, in the case of crystallised minerals, we generally have the actual object surviving through the ages. The liquid carbon dioxide imprisoned in a quartz crystal, or the tiny zircon surrounded by its halo in mica, have been there for untold centuries and survive to tell the tale of their own history. The same is true of the radioactive mineral, which by its present composition gives a clue to past changes; the structure of the crystal remains as a permanent record of its original nature. We have in our hands the very object that existed millions of years ago, and not merely a cast of it, and we can continue on it the processes that nature has begun. The forces of crystallisation that brought together its component elements have held them together in the same relative positions, of which the unchanged form is the guarantee.

This circumstance gives a peculiar interest to the study of minerals; it is one which impresses a feeling of awe and fascination akin to that aroused by an ancient manuscript or a work of art which survives as a permanent record of the artistic life and thought of bygone ages, and, further, it invests them with a unique value for the decipherment of the past.

There is one other aspect of mineralogy which I wish to emphasise. I have directed attention to the fatal sort of specialisation and exclusion to which the natural history school of thought tended; but let me repeat that mineralogy is, nevertheless, a branch of natural history, and that the proper study of minerals, as of all natural objects, is in itself a safeguard against specialisation.

The true mineralogist must bring to this pursuit the resources of all the sciences; one who is merely concerned with the physics or chemistry or crystallography of minerals makes only a one-sided study of the subject. The more intense and concentrated the work of the true mineralogist, the less confined will it be: in fact, the

more he specialises in mineralogy, the less of a specialist does he become.

For this reason, the natural history subjects have a very particular educational value; they deserve to hold their own for educational purposes, and not to be broken up into specialised sections. They have a particular value, not only as a stimulating introduction to chemistry or physics or biology as taught in schools to beginners, but also as a means of maintaining interest in those sciences at a later stage.

In young children, the instinct for collecting is strong, and equally strong is the desire to know something about what they collect; by many of them, the approach to science is most easily made through an interest in natural history.

At the later stage, many older boys and girls on the literary side in the upper forms of schools, whose main interest is outside science and who realise that it will not play a large part in their lives, boys and girls to whom prolonged teaching of chemistry, physics, and biology (especially if they are separated by water-tight compartments) will be uninteresting, and therefore largely unprofitable might be made to retain their hold on the principles of all these fundamental sciences through the study of natural history.

We shall surely do well to utilise any interest that brings home to ordinary students the knowledge and conviction that science is not merely laboratory work, but that its principles are to be found in operation everywhere, though they may have to be explored in the laboratory. Those who specialise in language or history or literature must acquire this conviction by experience, just as those who specialise in science must learn by experience that all great literature is the expression of ideas, and that even scientific ideas cannot be expressed by an illiterate use of language.

A judicious employment of natural history will, I believe, do much to establish science in the place that it should occupy in our educational system.

When I accepted the invitation of the Council to deliver this lecture, I welcomed the opportunity it would give me of recalling to the Chemical Society this aspect of my favourite pursuit.

And, let me add, even for scientific workers in their later years a taste for natural history in any of its branches is worth maintaining as a very real corrective to narrow specialisation.

If an illustration be required, I cannot do better than remind you again of the wide scientific interests and achievements of the remarkable man whose name this lecture bears.

Mineralogy and botany appealed to his wide and catholic taste;

his love for minerals and plants was an abiding possession to him, not only because he loved them as beautiful things, but because he was a man deeply interested in natural objects and in the secrets of science that are revealed by them.

To those whose work lies in laboratories, such intercourse with nature is easily maintained, for there are many pathways that lead from experimental science to natural history.

Like Antaeus, they can always strengthen themselves by contact with Mother Earth, feeling with Wordsworth:

> "that Nature never did betray
> The heart that loved her; 'tis her privilege
> Though all the years of this our life to lead
> From joy to joy."

XXXII.—*The Synthesis of Ammonia at High Temperatures. Part II.*

By Edward Bradford Maxted.

In a recent paper (this vol., p. 168), the equilibrium between nitrogen, hydrogen, and ammonia at high temperatures was discussed from a thermodynamical point of view, and evidence was brought forward showing that in all probability the ammonia content of such a gas mixture in equilibrium, after decreasing with increasing temperature, eventually passes through a minimum and finally rises once more. On the basis of this theoretical indication of the possibility of a thermal synthesis of ammonia, it was shown experimentally that considerable yields of ammonia may be obtained by cooling a mixture of nitrogen and hydrogen extremely rapidly from the temperature of the oxy-hydrogen flame to that of the room.

In continuation of the above work, and especially in view of the known fact that a mixture of nitrogen and hydrogen may be completely converted into ammonia by sparking in a eudiometer over dilute acid (Donkin, *Proc. Roy. Soc.*, 1873, **21**, 281), an investigation was begun of the yields of ammonia obtainable from a rapidly cooled, high-tension arc, also by sparking, the present paper being a summary of the results obtained by induction discharge modified in such a way as to constitute a small, high-tension arc burning within a capillary tube, through which the mixture of nitrogen and hydrogen was passed.

By confining the action to a capillary tube, in the manner

described, the gas to be treated may be brought uniformly into contact with the discharge, and it was found easily possible to obtain at atmospheric pressure yields of ammonia amounting to 1·5 per cent. by volume of the gas-mixture taken for treatment. Induction sparks, as such, were found to exert a comparatively feeble action on the synthesis, energetic formation of ammonia only taking place when the electrodes were brought sufficiently close together to transform the ordinary spark discharge into a small, high-tension arc, accompanied by a visible and apparently continuous flame of high temperature.

Experimental.

The apparatus employed for the series of experiments about to be described consisted of a capillary glass tube having an internal diameter of 0·65 mm., an external diameter of 5 mm., and a length of about 10 cm. Platinum wire electrodes, 0·25 mm. thick, were sealed into the capillary tube in such a way as to leave a spark-gap of the size required, whilst the passage of gas through the tube was effected by means of fused-on glass side-tubes.

It was found inadvisable, on account of frequent fractures, to employ a heavy discharge, the most satisfactory conditions for the investigation being obtained with a "two-inch" coil, supplied with a primary current of from 3 to 3·5 amperes from the laboratory 220-volt main. Pure hydrogen and nitrogen for the synthesis were mixed in the proportion of three to one in a large gasholder and compressed into a cylinder for convenience in use. This mixed gas was passed at carefully determined rates through the capillary spark-gap, the ammonia formed being absorbed in dilute acid and estimated by means of Nessler's solution.

The first point to be investigated was the influence of the size of the spark-gap on the yield of ammonia, this gap being varied from 10 to 0·5 mm. while the rate of passage of the gas was first kept constant at 40 c.c. per hour, and, secondly, varied in such a way that the time of contact was kept at 0·0015 second for spark-gaps of various sizes. Table I summarises the results obtained by the first of these two methods, namely, with a constant rate of flow, table II those obtained by the second, that is, with a constant time of contact with the spark-gap, the primary current being in every case 3·5 amperes at 220 volts.

TABLE I.

Rate of Flow of Hydrogen–Nitrogen Mixture 40 c.c. *per hour.*

Length of spark-gap in mm.	Nature of discharge.	Percentage of ammonia by volume in issuing gases.
10	Spark	0·1
5	Incipient flame	0·25
1·5	Arc flame	0·8
0·5	Arc flame	1·1

TABLE II.

Estimated Time of Contact, 0·0015 *sec.*

Length of spark-gap in mm.	Nature of discharge.	Percentage of ammonia by volume in issuing gases.
10	Spark	less than 0·01
5	Incipient flame	0·04
1·5	Arc flame	0·5
0·5	Arc flame	1·1

It will be seen that as the size of the spark-gap is decreased, the flame loses its well-defined spark-like character and becomes a small but intensely hot high-tension arc, this flame, probably by virtue of its high temperature combined with the rapid cooling effect afforded by the relatively cold walls of the glass capillary tube, possessing the power of inducing the combination of nitrogen and hydrogen to an extent obtainable otherwise only by the action of a catalyst under a high pressure. The rate of flow of the nitrogen–hydrogen mixture through the capillary tube was measured by allowing the gas issuing from the reaction tube to pass through a small, specially constructed gas-washing bottle, in which the ammonia was absorbed by very dilute sulphuric acid, the number of bubbles which formed per minute being counted and the volume of a bubble being known. The estimation of ammonia in the resulting solution was carried out by means of Nessler's reagent.

It is difficult to estimate the temperature of the small high-tension arc formed, which, however, for the purpose of obtaining rough comparative figures for the various times of contact, has been assumed to be at approximately 3000°, but the effect of increasing temperature on the yield of ammonia formed is clearly seen. This rise in yield with increasing temperature at high temperatures (in contradistinction from the decrease obtained at moderate temperatures) agrees with the results already reported. When working with small spark-gaps, a considerable deposit of platinum, removed from the electrodes by volatilisation and other

means, was obtained on the sides of the capillary tube, and in some cases the tube became fractured by the intense local heat, although in general the tube itself remained moderately cool, and in any case showed no tendency to soften.

The above results having demonstrated the necessity for employing as small a spark-gap as possible, in order to obtain the maximum local heating effect and consequently the maximum yield of ammonia, the effect of varying the time of contact with a spark-gap of constant small length (0·5 mm. and 1·5 mm.) was investigated. With an exceedingly small arc of the nature described, sufficiently rapid cooling for the retention of the ammonia formed is readily obtained by the action of the tube itself, the difficulty being rather the uniform heating to arc temperature of the comparatively rapid current of gas.

Table III demonstrates this point, it being found that any increase in the time of contact of the gas with the small arc, within the limits studied, causes a corresponding rise in the ammonia-content of the issuing gas.

TABLE III.

	Spark-gap in mm.	Velocity of flow in c.c. per hour.	Estimated time of contact in seconds.	Percentage of ammonia by volume in issuing gases.
(*a*)	0·5	97·2	0·0006	0·7
	0·5	40·5	0·0015	1·1
	0·5	18·9	0·0032	1·4
	0·5	15·0	0·0041	1·5
(*b*)	1·5	670·0	0·00027	0·25
	1·5	130·0	0·0014	0·5
	1·5	64·8	0·0028	0·6
	1·5	34·8	0·0052	0·87

The above results appeared to offer considerable encouragement for the investigation of the formation of ammonia by rapidly cooled high-tension arcs of a larger size. The results of such work will be communicated in a later paper.

[*Received, March 21st*, 1918.]

XXXIII.—*Atomic and Molecular Numbers.*

By HERBERT STANLEY ALLEN.

ATOMIC NUMBERS.

ATOMIC weight and its determination have occupied a prominent position in the work of chemists since Dalton first put forward the Atomic Theory. Recent investigations in connexion with radio-

active elements and lead derived from radioactive substances have proved that the atomic weight has not the unique value hitherto attributed to it, and that a chemical element, such as lead, may be a mixture of "isotopes" occupying the same place in the periodic classification, but inseparable by chemical methods. Increasing importance is now being attached to the atomic number of an element, that is, the number which denotes the position of the element in Mendeléev's periodic table. As is well known, there are a few instances in which the place of the element is not in agreement with the atomic weight determinations; in such cases, the atomic number is given the value appropriate to the place in the table assigned by the chemical or physical properties. The values of the atomic numbers now accepted are given in table I, which follows the periodic classification of the elements commonly adopted. A better representation of the facts is obtained by employing a spiral in three dimensions. In this case, hydrogen may be placed at the pole of the spiral.

According to the electrical theory of matter, the atom consists of a central nucleus or core, carrying a resultant positive charge, surrounded by rings of negative electrons. It was first suggested by van den Broek that the number of the place in the periodic table was the same as the number of electrons in the atom or the number of unit charges carried by the nucleus. The same suggestion was made shortly afterwards by Soddy in connexion with the radioactive changes in the last thirteen places in the periodic table. The hypothesis is confirmed by the measurements of Barkla on the intensity of the X-radiation scattered from various substances. These indicate 7 electrons per atom of N, 8 for O, 6 for C, 16 for S, 1 for H. Rutherford's work on the scattering of α-particles by atoms of matter led him to the conclusion that the concentrated nuclear charge was approximately equal to half the atomic weight multiplied by the charge of an electron. The atomic numbers are, in fact, roughly equal to half the atomic weight.

It was, however, through the work of Moseley on the frequency of vibration of the X-rays, which are characteristic of the elements, that the importance of the atomic numbers was firmly established. The square root of the frequency of a line in the X-ray spectrum was found to be proportional to a number which increased by unity in passing from one element to the next in the periodic table. Thus every element from aluminium to gold may be characterised by an integer, N, which determines its X-ray spectrum. These atomic numbers were tabulated for the elements in question on the assumption that N for aluminium is 13. Between uranium and hydrogen, only five places remain vacant. For the rare earths,

PERIODIC SYSTEM OF THE ELEMENTS.

O	I	II	III	IV	V	VI	VII	VIII
	H 1							
He 2	**Li 3**	**Gl 4**	**B 5**	**C 6**	**N 7**	**O 8**	**F 9**	
Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	
A* 18	**K* 19**	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26 Co* 27 Ni* 28
	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	
Kr 36	Rb 37	Sr 38	Yt 39	Zr 40	Cb 41	Mo 42	—43	Ru 44 Rh 45 Pd 46
	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te* 52	I* 53	
Xe 54	Cs 55	Ba 56	The 57 — Rare Earths					
					Ta 73	W 74	- 75	Os 76 Ir 77 Pt 78
	Au 79	Hg 80	Tl 81	Pb 82	Bi 83			
Nt 86		Ra 88		Th 90		U 92		

* Elements not placed in the order of the atomic weights.

which have not been tabulated in table I, Moseley found the following values for N: La, 57; Ce, 58; Pr, 59; Nd, 60; Sa, 62; Eu, 63; Gd, 64; Ho, 66; Er, 68.

It may now be regarded as certain that most of the properties of the elements depend on the value of the atomic number rather than on that of the atomic weight. For example, the atomic frequency which determines the thermal behaviour of the element in the solid state has been shown by the author (*Proc. Roy. Soc.*, 1917, [*A*], **94**, 100; *Phil. Mag.*, 1917, [vi], **34**, 478, 488) to bear a simple relation to the atomic number. Certain electronic frequencies are related to the atomic number in a similar way.

It will be noticed that Moseley's work does not give an unique determination of the value of N, since it is based on the assumption that N is 13 for aluminium. Rydberg has suggested that two unknown elements should be included in the periodic table between hydrogen and lithium, so that the atomic number of lithium would be 5 instead of 3. For all the elements later in the table, Rydberg's ordinals would be greater than Moseley's numbers by 2 units. Evidence in favour of Moseley's numbers is accumulating. Thus Barkla's results on the scattering of *X*-rays by air show that the number of electrons is as near to 7 for an atom of nitrogen as it is possible to estimate the pressure of the air under which the experiments were made. In the work of the present author on the relation between atomic frequency and atomic number, it was found that the atomic numbers of Moseley gave more satisfactory agreement than did the atomic ordinals of Rydberg. The same conclusion was arrived at by van den Broek (*Phil. Mag.*, 1914, [vi], **28**, 630).

The atomic numbers express in a compact form many facts that have been long familiar to students of chemistry. They afford a striking confirmation of the statement of Chancourtois, made in 1863: "The properties of the bodies (elements) are the properties of number." Newlands assigned to the elements numbers (from 1 to 56) to indicate the order in which the elements must be placed when arranged in the ascending order of their atomic weights. He put forward the "law of octaves," according to which the numbers for members of the same family will differ by 7, or some multiple of 7, provided that the elements are not consecutive. Newlands admitted that it might be necessary to alter the number (7) separating analogous elements to some higher figure should a large number of new elements be discovered (compare Garrett, "The Periodic Law," 1909, Ch. III.). An examination of the atomic numbers of table I shows that in many cases the difference between the numbers for members of the same family is either 8

or some multiple of 8. In other cases, however, the difference is found to be 18. Thus in the case of the inert gases of the zero group, the atomic numbers for He (2), Ne (10), A (18) show differences of 8, whilst A (18), Kr (36), and Xe (54) show differences of 18. The interval between Xe (54) and Nt (86) is $32 = 4 \times 8$. In the case of subsidiary families of the same group, a common difference of 10 is manifest, for example, K (19), Cu (29), or Rb (37), Ag (47). The reason for these variations from the more commonly observed difference of 8 is the presence of three elements (for example, Fe, Co, Ni) instead of a single element in Group VIII of the table. The two extra elements change the common difference from 8 to 10 or from 16 to 18. Thus the law of octaves must be replaced by a new rule, which may perhaps be termed the rule of eight—a rule, however, to which there are quite definite exceptions (1) in the consecutive elements of Group VIII, (2) in the elements displaced two units by Group VIII, (3) in the metals of the rare earths.

Molecular Numbers.

The author has suggested the introduction of the term "molecular number" to signify the sum of the positive charges carried by the atomic nuclei contained in the molecule. Thus the molecular number bears the same relation to the atomic number as the molecular weight bears to the atomic weight. When a molecule contains a atoms of an element A, b atoms of B, and c atoms of C, its chemical formula may be written $A_aB_bC_c$, whilst its molecular number will be $N = aN_a + bN_b + cN_c$, where N_a, N_b, N_c are the atomic numbers of the component elements. For example, the molecular number of water (H_2O, hydrol) is 10, for the molecule contains two atoms of hydrogen (nuclear charge, 1) and one atom of oxygen (nuclear charge, 8). Thus the C.G.S. system of units is a decimal system in a deeper and more intimate sense than its originators supposed, for it is based on the assumption that the gram is the mass of 1 c.c. of water at the temperature at which its density is a maximum. This fact probably accounts for the remarkable numerical relations, involving powers of 10, which the author has shown to exist between certain fundamental physical constants (*Proc. Physical Soc. London*, 1915, **27**, 425).

The four compounds, CH_4, NH_3, H_2O, HF, formed by the combination of hydrogen with a "typical" element belonging to successive groups in the second series of the periodic table, all have the same molecular number, 10. The corresponding elements in the third series of the table form compounds with hydrogen of the

same type, SiH_4, PH_3, H_2S, HCl, all having the molecular number 18 (=10+8).

It may be remarked here that the molecular number is usually, but not invariably, an even number. This arises from the fact that when the valency is odd, the atomic number is usually odd also; but in the case of an element, such as copper, which may be either univalent or bivalent, or in the case of some of the metals of Group VIII the molecular number may be odd.

We have seen that the atomic numbers of analogous elements usually differ by 8 or a multiple of 8, or in some cases by a number that is 2 units greater than one of the foregoing. It is obvious that results of a similar character are to be expected in dealing with the molecular numbers of analogous compounds. The halogen compounds of the alkali metals may be considered by way of illustration. The results are collected in table II, the figures in italics being the differences between the molecular numbers in adjoining rows or columns.

TABLE II.

Element.	F 9 Fluoride.		Cl 17 Chloride.		Br 35 Bromide.		I 53 Iodide.
Li 3	12	*8*	20	*18*	38	*18*	56
	8		*8*		*8*		*8*
Na 11	20	*8*	28	*18*	46	*18*	64
	8		*8*		*8*		*8*
K 19	28	*8*	36	*18*	54	*18*	72
	18		*18*		*18*		*18*
Rb 37	46	*8*	54	*18*	72	*18*	90
	18		*18*		*18*		*18*
Cs 55	64	*8*	72	*18*	90	*18*	108

The molecular number of a cuprous haloid exceeds by 10 that of the corresponding potassium compound, and similarly the molecular number of a silver haloid exceeds by 10 that of the corresponding rubidium compound.

In the case of an element which has a valency greater than 1, the results may be more complicated, since one or more of the atomic numbers may require multiplication by a numerical factor depending on the number of atoms in the molecule. For compounds containing only elements from N=1 to N=25, however, comparatively simple results will be obtained, since the divergences due to the three elements in Group VIII do not then appear.

Instead of the law of octaves, we have what has been termed the rule of eight holding, with certain exceptions, in connexion with the molecular numbers of analogous compounds.

The value of N for a compound radicle can be calculated in the same way as for a complete molecule. Thus for the ammonium group (NH_4), the value of N, which may be called the group

number or the radicle number, is 11. It is noteworthy that this is the same as the atomic number of sodium, which can be replaced by the ammonium group in so many of its compounds. The principle here involved may be extended, and we may say that in a chemical compound one radicle may frequently be replaced by another having the same number, or a number differing from the first by 8 or a multiple of 8.

The hydrogen molecule, H—H (N = 2), may be regarded as the typical simple molecule, from which a large number of chemical compounds may be derived by substituting for one or both of the hydrogen atoms another atom or radicle.

Thus water may be looked on as a typical compound in which one atom of hydrogen (N = 1) is combined with the hydroxyl group, OH (N = 9). The hydroxyl group may be replaced by CH_3, NH_2, F, for each of which N = 9, giving rise to the compounds methane, ammonia, and hydrogen fluoride. Again, in each of these compounds the hydrogen atom may be replaced by one of the groups mentioned, giving rise to such compounds as C_2H_6, $CH_3{\cdot}OH$, N_2H_4, $NH_2{\cdot}OH$, H_2O_2, for which the molecular number is $9+9=18$.

Owing to the fact that the group number of $\cdot CH_2\cdot$ is 8, the rule of eight is prominent in the case of organic compounds. In open-chain compounds, the addition of each CH_2-group means an increase of 8 in the molecular number.

It is necessary to enter a caution as regards the interpretation of the results when dealing with a chemical group or radicle. The "group number" may be taken to represent the sum of the charges of the atomic nuclei of the group. It will only represent the number of negative electrons associated with the radicle as well when the radicle, considered as a whole, is not charged or electrically neutral. According to the views of Sir J. J. Thomson (*Phil. Mag.*, 1914, [vi], **27**, 768), the radicle may be charged either positively or negatively, and in such a case the number of negative electrons will differ from the radicle number here given.

The molecular numbers here discussed, and the relations between them, are not mere arithmetical curiosities. It is to be remembered that the molecular number is associated with a perfectly definite physical conception, namely, the number of unit charges found in the positive nuclei of the atoms in the molecule or the number of the complementary negative electrons. It is to be anticipated that the molecular numbers will play an important part in determining the physical or chemical characteristics of molecules or radicles. Some progress, in fact, has already been made in establishing such a connexion. It has been shown by Nernst and others that the thermal behaviour of a compound in

the solid state depends on a certain characteristic frequency or frequencies. The author has found (*Phil. Mag.*, 1918, [vi], **35**, 338) that simple relations exist between the products obtained by multiplying such a frequency and the molecular number of the compound. Thus there must be an intimate connexion between the specific heat and the molecular number. In the author's opinion, it is safe to predict that other physical properties of chemical compounds will be found to depend on the values of the molecular numbers.

KING'S COLLEGE,
UNIVERSITY OF LONDON.

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XXXIV.—*Reactions between Solid Substances.*

By LESLIE HENRY PARKER.

IN a previous communication by the author (T., 1914, **105**, 1504), it has been shown that under certain conditions it is possible to bring about interaction between various pairs of solid substances by means of shearing stress, even at ordinary temperatures, or at least very greatly to increase the velocity of these reactions above that which normally pertains at these temperatures. The experiments described in that paper led the author to the conclusion that shearing stress, such as could be applied by hand between a pestle and mortar, is widely different in its effects from simple pressure, and that one of the main reasons why it is able to bring about reactions between apparently solid substances is that local or surface fusion of the reacting substances is occasioned.

This phenomenon seemed of sufficient interest to warrant further study, as it is a well-known fact that salts in the fused state are capable of reacting together.

In considering the conditions under which solid salt pairs are capable of reacting, it has to be remembered that most of the ordinary salts melt at a temperature that is high compared with that at which one commonly works with these substances; moreover, that a slight rise in temperature very often occasions a very rapid increase in the reaction velocity between two substances. From this it follows that the readiness with which two salts react in the fused state may be due to the influence of one or both of the following factors, namely, (1) the *high temperature* necessary

to bring one or both of the salts into a state of fusion, or (2) the existence of one or both of the salts in the *liquid state*, and the intimate contact occasioned thereby.

The object of the present investigation was to attempt to gain some idea of the relative importance of these two factors, because if high temperature is the main influence in causing two salts to react, some further agency must be looked for than mere fusion when reactions are brought about under shearing stress. If, on the other hand, the existence of the liquid state is the predominating influence, there appears to be no reason why salts should not react with appreciable velocity at ordinary temperatures should one or more of them be brought into a state of fusion, however transitory.

An investigation was therefore commenced on the velocity of reaction between various salt pairs at temperatures up to and through the melting point of the mixtures. The form of the curve obtained by plotting velocity of reaction against temperature should give information on the point desired.

Let us suppose that the temperature is the main influence in accelerating the velocity of reaction. The latter will go on increasing as the temperature rises until the melting point of the mixture is reached. At this point, however, there should be no marked increase in velocity, as we have assumed the existence of the liquid state to be of secondary importance. The curve should therefore exhibit no discontinuity at this temperature, but pass smoothly through the melting point.

On the other hand, let us suppose that the existence of the liquid state is of greater importance to the progress of the reaction. There may be, and probably will be, an increase of reaction velocity between the two mixed salts while still both in the solid state. When the point of fusion of the mixture is reached, however, there will be a sudden increase in the reaction velocity, and the curve will exhibit a sudden break at this temperature.

Experimental.

Sodium Carbonate and Barium Sulphate.

The interaction between these substances has already been investigated under shearing stress, as described in the previous paper (*loc. cit.*).

10·6 Grams of sodium carbonate, prepared from purified sodium hydrogen carbonate and dried by prolonged heating, were mixed with 23·34 grams (equivalent quantity) of barium sulphate, precipitated from purified barium chloride, and dried by heating in a current of dry air. The two salts were placed in a dry, air-tight

bottle, stirred with a glass rod, and shaken for fifteen minutes to mix them thoroughly. An arbitrary sample of this mixture was then taken for analysis.

A quantity equivalent to 1·06 grams of sodium carbonate (3·394 grams) was weighed out, treated with cold water, and lixiviated through a specially prepared Gooch crucible, the filtrate being treated with *N*- and *N*/10-hydrochloric acid, as previously described (*loc. cit.*). An amount of acid was neutralised corresponding with exactly 1·06 grams of sodium carbonate, showing that the original mixture was homogeneous and not affected by water. If sufficient care were taken to ensure that the salts were in a fine state of subdivision, and that they were stirred (not ground) and shaken together sufficiently, this method of sampling gave a similar result with many other experiments. No variation in the composition of the mixture in various parts was therefore to be feared, especially as only sufficient mixture was made up at any one time for nine experiments and one sample.

A nickel boat was then constructed to accommodate, when about half full, 3·394 grams of the mixture. This was heated to various temperatures for various lengths of time in an electric furnace, constructed by winding about 900 cm. of nichrome wire (4·1 ohms per metre) on 20 cm. of opaque silica tubing of 4·4 cm. internal bore. This was insulated with about six turns of asbestos paper and two turns of asbestos cloth. The ends were closed with asbestos card, and the whole was connected with a 110-volt lighting circuit, when suitable temperatures, as registered by a thermo-element, could be obtained and adjusted by variable resistances.

The procedure for each experiment was to heat the furnace to the required temperature, open one end, quickly insert the boat

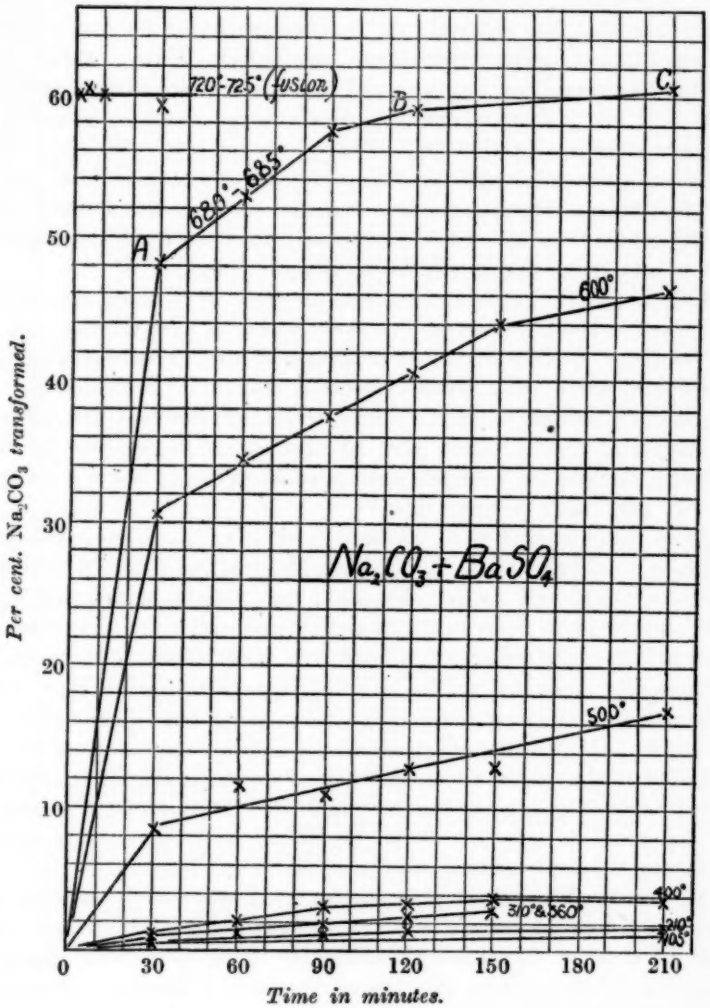
TABLE I.

Time in minutes.	Sodium carbonate transformed. Per cent.							
	105°	210—215°	310°	360°	400°	500°	600°	680—685°
30	0·55	0·48	1·07	0·96	1·37	8·42	30·5	48·1
60	1·37	0·30	1·31	1·25	2·27	11·7	34·4	52·8
90	—	1·19	1·97	2·26	3·34	11·1	37·6	57·6
120	—	1·37	2·62	—	3·64	13·1	40·6	58·8
150	0·55	—	2·98	—	3·94	13·2	44·0	—
180	—	1·79	—	—	—	—	—	—
210	1·37	1·79	—	2·86	3·76	17·4	46·3	60·6

	700—720° (fusion).
2	60·0
5	60·6
10	60·0
30	59·2

containing the mixture, so adjusting its position in the middle of the furnace on some silica supports that it was clear of the walls of the furnace and almost touching the thermo-element, and close the furnace for the required time. At the expiration of a definite

FIG. 1.



period, the boat was withdrawn and the residual sodium carbonate was estimated. The results are shown in the table on p. 398.

These results are expressed graphically in Fig. 1.

It will be noticed that this mixture fuses at about 720° (as

registered by the thermo-element used), and in this state the velocity of reaction, so far as can be seen, is practically instantaneous, equilibrium being set up for the reaction

$$Na_2CO_3 + BaSO_4 \rightleftharpoons BaCO_3 + Na_2SO_4$$

when about 60 per cent. of the sodium carbonate is transformed.

It will also be remarked that up to 400°, the amount of sodium carbonate that has entered into reaction with the barium sulphate is insignificant, even after three and a-half hours. What little double decomposition has occurred has taken place fairly regularly, and it is fairly easy to compute the average reaction velocity for the temperatures up to 400°. The curves for 500°, 600°, and 685°, however, show some peculiarities. It will be noticed that during the first thirty minutes, in each case the reaction has started fairly rapidly, but after this time, has slowed down to a regular velocity, the points lying practically on a straight line.

This might be explained by the presence of a trace of moisture occluded in the particles of the salts, which is always very difficult to remove. At the high temperature of the experiments, this is rapidly expelled, but causes a certain amount of reaction between the salts on its own account. Once driven off, however, its influence is lost, and the straight part of the curve represents the true velocity of reaction between sodium carbonate and barium sulphate at any particular temperature.

It is possible that this moisture may have occasioned the small amount of change at the lower temperatures, and that had it been possible completely to dry the salts, the velocity of reaction up to 400° would have been negligible. In the curve for 685°, the portion between the points *A* and *B* has been taken as representing the reaction velocity, as the point *C* represents equilibrium, which was probably attained before the time represented in the figure (210 minutes). If we now plot reaction velocity against temperature, we obtain the curve shown in Fig. 2 (continuous line), which is remarkably regular up to the point for 720°, when, the velocity of the reaction at that point becoming instantaneous, a sudden break in the continuity of the curve occurs.

If the equilibrium of this system is considered, it will be seen that in the solid state there are present four solid phases, which can be defined by three components. This gives one degree of freedom for the system, and the equilibrium is therefore determined by the temperature; it is therefore probable that there is a definite equilibrium mixture for each temperature, and that the lower curves in Fig. 1 would not all of necessity approach the equilibrium attained on fusion, namely, the transformation of 60 per cent. of the sodium carbonate.

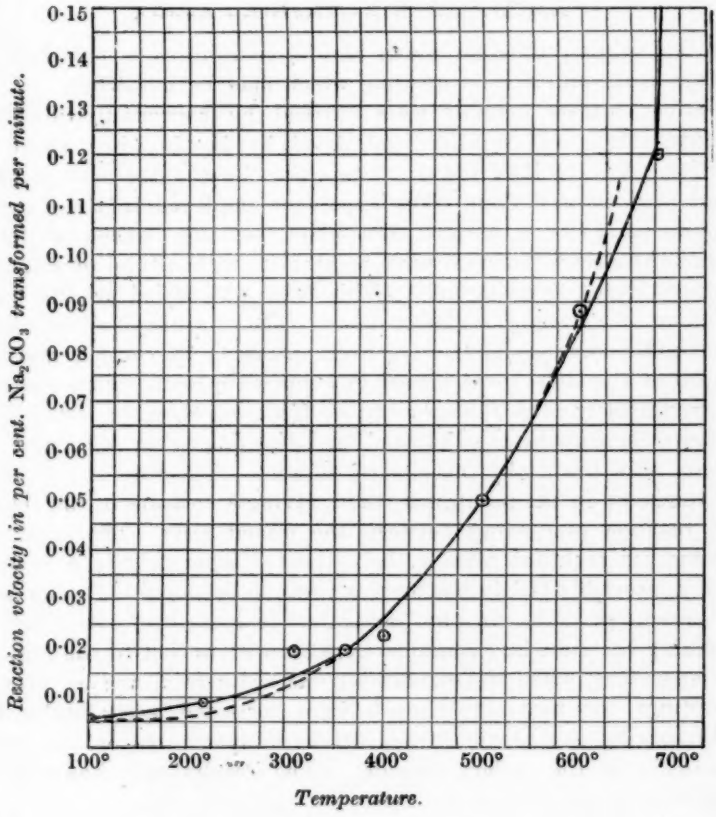
It was also endeavoured to reconcile the velocity–temperature curve in Fig. 2 with the formula put forward by Arrhenius and van't Hoff, namely,

$$\frac{d \log k}{dT} = \frac{A}{T^2} + \frac{B}{T} + C.$$

The dotted curve in Fig. 2 is that given by the formula

$$\log k = \frac{1988}{T} + 11{\cdot}24 \log T - 36{\cdot}332.$$

FIG. 2.



which follows the experimental curve very closely except at the higher temperatures as the point of fusion is approached.

The next two cases were chosen to be of such a nature that no limiting equilibrium could be obtained, it being possible for the reaction to proceed to completion in one sense.

Silver Nitrate and Sodium Carbonate.

The products of this interaction are silver carbonate and sodium nitrate, and as the former is unstable, decomposing with rapid evolution of carbon dioxide at 100°, the rate of evolution of this gas from a mixture of silver nitrate and sodium carbonate could be used as a measure of the velocity of reaction between these two salts. The reaction may be regarded as capable of proceeding to completion in the sense

$$Na_2CO_3 + 2AgNO_3 = 2NaNO_3 + Ag_2CO_3,$$

as the only equilibrium which can be established is that between silver oxide and carbon dioxide, which may be neglected.

Silver nitrate crystals were purified by recrystallisation from dilute nitric acid solution and dried by heating just above the fusion point for two hours. The sodium carbonate was prepared and purified as before. The apparatus employed in these experiments consisted of a thick Jena-glass test-tube, somewhat longer than the electric furnace used to heat it, with a tube of soft glass ground into its open end. This tube was sealed to the gauge column of a Sprengel exhaust pump. The mixture of silver nitrate and sodium carbonate (always 1·699 grams of the former and 0·53 gram of the latter) was placed in a porcelain boat, which was then introduced into the Jena-glass tube. This was then connected to the pump, the apparatus exhausted, and the Jena-glass tube and contents were heated by the electric furnace. The rate of fall of the manometer on the pump was noted, giving a measure of the velocity of reaction proceeding between the mixed salts. The salts were tested for occluded gases by being heated separately in a vacuum. No appreciable fall in the mercury was to be noted. In any series of readings taken at any particular temperature, after the last reading the tube and contents were allowed to cool to the ordinary temperature, when the manometer was again read, and all previous readings for that experiment were corrected accordingly, thus eliminating the effect of the various temperatures on the partial pressure of the carbon dioxide. The results are shown in the table on p. 403.

These results are expressed graphically in Fig. 3.

The characteristics previously noted are again in evidence. After a short period of induction over the first five minutes, due no doubt to the gradual heating up of the mixture, the curves for the temperatures between 110° and 170° show an increasing rapidity for the reaction at the start, over a period of about a

TABLE II.

Time in minutes.	Corrected partial pressure of carbon dioxide in mm. of mercury.					
	90°	110°	130°	155—160°	165°	170°
10	—	—	0·5	1·8	2·7	15·3
15	—	—	—	—	12·6	30·6
20	—	—	4·5	12·9	22·4	42·3
25	—	—	—	—	28·6	50·4
30	1·0	5·5	9·5	20·2	34·0	53·7
60	1·8	12·7	17·2	32·2	43·8	63·0
90	3·7	15·8	20·0	37·7	48·3	69·3
120	—	17·0	—	41·4	52·8	—
150	5·5	18·0	29·0	45·0	57·4	77·4
180	—	19·0	29·0	46·0	60·0	81·0
210	8·2	—	—	—	—	—
270	9·6	—	—	—	—	—
300	10·5	—	—	—	—	—

Time in minutes.	Corrected partial pressure of carbon dioxide in mm. of mercury.	
	180° (fusion).	240—250° (fusion).
5	3·2	1·8
6	7·2	3·7
7	13·6	6·4
8	25·4	10·1
9	59·7	14·7
10	97·0	26·6
10½	112·0	43·1
11	125·0	62·4
11½	135·0	89·0
12	146·0	114·0
12½	157·0	134·0
13	168·0	153·0
13½	180·0	170·0
14	191·0	186·0
14½	202·0	205·0
15	211·0	221·0
15½	219·0	237·0
16	225·0	
16½	230·0	
17	235·0	
17½	239·0	
18	243·0	
19	247·0	

further fifty minutes. After that time, the rate of reaction in each case becomes practically uniform.

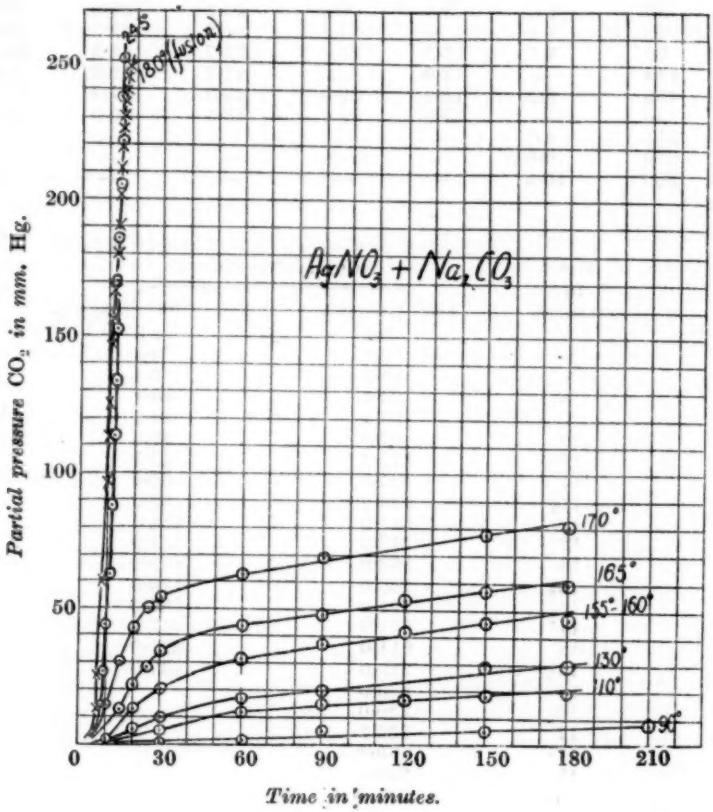
The curves for 180°, where fusion took place, and for 245°, although apparently almost coincident on the diagram at the scale given, are by no means so in reality. Calculated from the figures in table II, the curve for 245° represents almost twice the reaction velocity as does the curve for 180°.

The graphical representation of reaction velocity against tempera-

ture is shown in Fig. 4, and again a sudden increase is to be noted at the temperature of fusion.

In the solid state, there are here present five phases, comprised of four solid phases ($AgNO_3$, Ag_2O, $NaNO_3$, Na_2CO_3) and one gaseous phase (CO_2); all these are defined by the four components Ag_2O, Na_2O, N_2O_5, and CO_2. The pressure of the system is there-

FIG. 3.



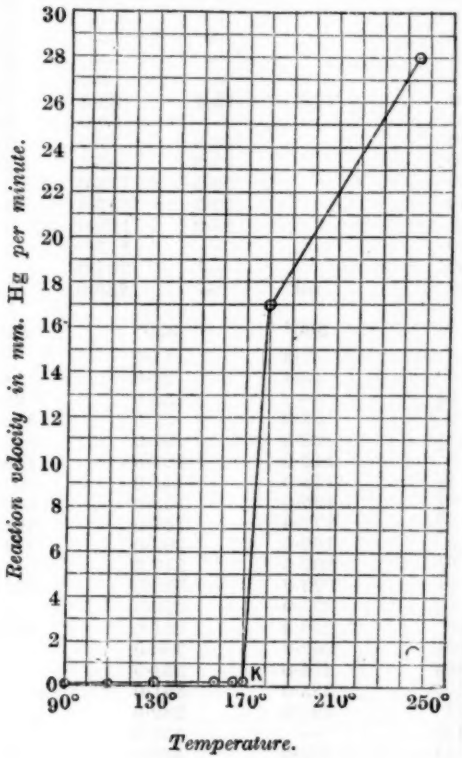
fore a function of the temperature, an example of the active masses of the reacting substances remaining constant in the solid state.

In the partly fused state there exist four solid phases, one liquid phase, and one gaseous phase, with the same number of components as before. There are, therefore, no degrees of freedom, and the point K is analogous to the triple point in the system ice-water-water vapour.

Cuprous Chloride and Sodium Carbonate.

This mixture was chosen more from the point of view of discovering what happened after fusion than actually at the fusion point. The cuprous chloride was prepared from the commercial substance by dissolving it in concentrated hydrochloric acid and pouring the solution into water. The precipitated salt was quickly

FIG. 4.



collected, washed with alcohol and ether, and dried for many hours at 100°.

It remained quite white, apparently indefinitely, in a dry, air-tight bottle. For each determination, a mixture of 0·991 gram of this salt with 0·53 gram of sodium carbonate was taken (equivalent quantities), and the experiments were conducted with the same apparatus as in the last reaction. The results are shown in the following table.

TABLE III.

Time in minutes.	Corrected partial pressure of carbon dioxide in mm. of mercury.			
	100°	150°	200°	260°
5		3·3	1·8	3·6
10		7·5	8·2	48·0
11		—	—	83·0
12		—	—	116·0
13		—	—	147·0
14		—	—	174·0
15		10·0	20·0	199·0
16		—	—	217·0
17		—	—	234·0
18		—	—	249·0
19		—	—	259·0
20		13·3	38·0	268·0
25		—	59·0	310·0
30		15·8	77·0	336·0
40		17·5	97·5	376·0
50		20·0	113·0	—
60		20·8	127·0	419·0
90		25·0	164·0	—
120		—	195·0	—
150		—	208·0	—
180	nil	—	230·0	—

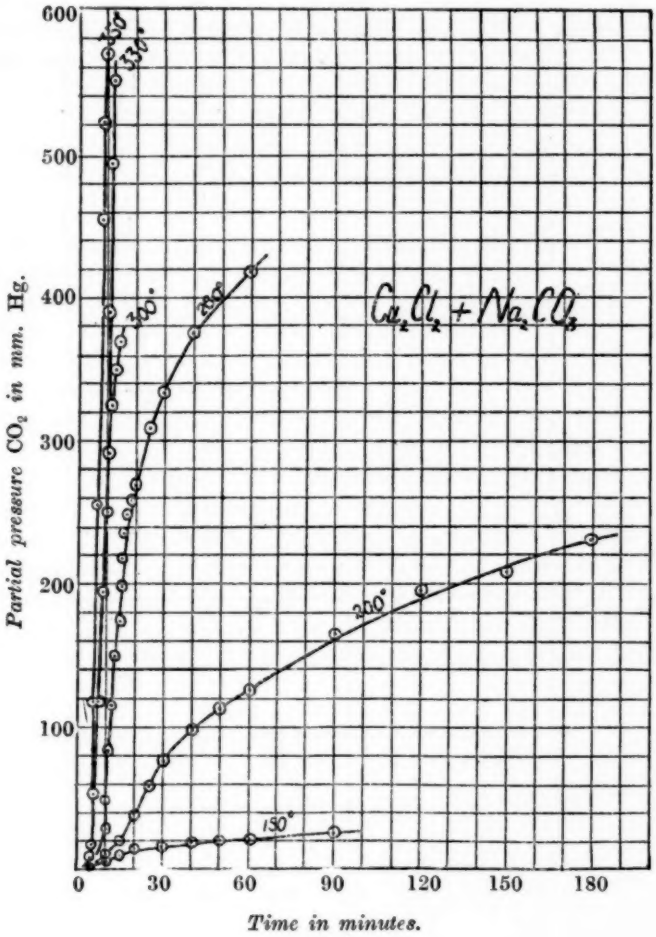
	300°	330°	350°
5	7·3	17·5	9·2
6	18·4	24·0	35·0
6½	—	35·0	68·0
7	53·0	53·0	119·0
7½	83·5	84·0	178·0
8	119·0	123·0	256·0
8¼	138·0	141·0	307·0
8½	155·0	163·0	353·0
8¾	172·0	181·0	404·0
9	192·0	200·0	454·0
9¼	207·0	217·0	—
9½	223·0	238·0	521·0
9¾	237·0	258·0	—
10	250·0	281·0	569·0
10¼	262·0	306·0	—
10½	274·0	334·0	—
10¾	283·0	361·0	—
11	291·0	389·0	—
11¼	—	420·0	—
11½	309·0	446·0	—
11¾	—	471·0	—
12	324·0	497·0	—
12¼	—	515·0	—
12½	338·0	531·0	—
12¾	—	548·0	—
13	350·0	—	—
13¼	362·0	—	—
14	370·0	—	—

These results are expressed graphically in Figs. 5 and 6.

Fusion took place at about 260°, causing a large increase in the reaction velocity.

It seems fairly well established, therefore, that the process of fusion of itself causes a marked increase in the reaction velocity of the mixtures, the ratio of velocity in the liquid state to that at the highest temperature in the solid state varying from infinity

FIG. 5.

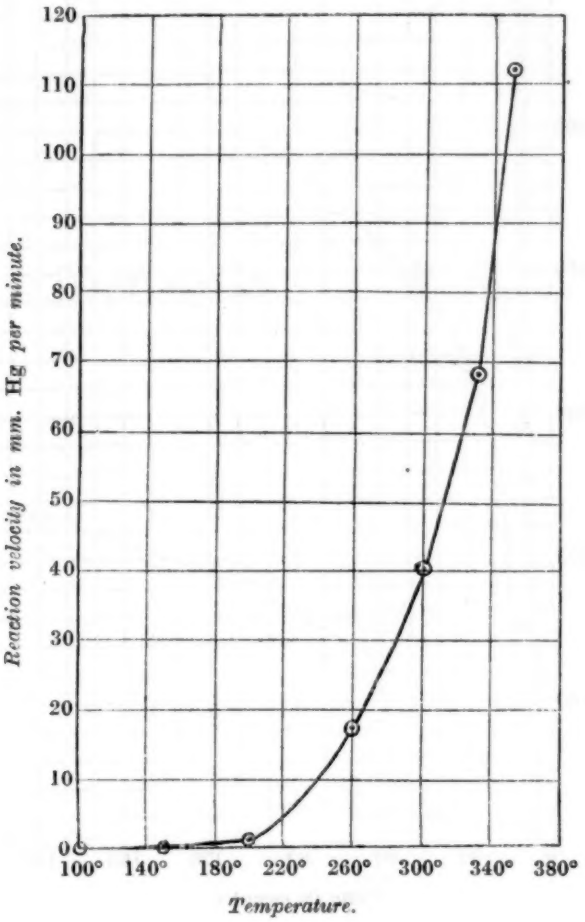


in Case 1, through about 150 in Case 2, to about 20 times in Case 3.

It may be taken, therefore, that the liquid state *per se* has a direct bearing on the interaction of salt pairs. It should be noted, however, that after fusion the velocity of reaction is not quite so

independent of the temperature as in the solid state. The velocity becoming practically infinite on fusion in Case 1, this could be investigated no further, but in Cases 2 and 3 it is seen that further rise in temperature causes a further great increase in reaction velocity, although not nearly so great as the increase pro-

FIG. 6.



duced by fusion over the velocity in the solid state. In Case 2, a rise of 65° nearly doubles the reaction velocity, and in Case 3, a rise of 90° multiplies the rate about six times. The reacting molecules now being in intimate contact, the temperature begins to exert a well-defined influence.

There seems therefore to be no inherent objection to the explanation, put forward in the previous communication, of the reactions brought about by shearing stress between apparently solid substances, namely, that the stress causes local or surface fusion of the salts; it has been shown that the liquid state, quite apart from temperature effects, has an important bearing on the capacity for interaction.

It is known that the size of particle may have a slight influence on the melting point of a substance, as in the case of salol investigated by Pavlov (*J. Russ. Phys. Chem. Soc.*, 1910, **40**, 1022), who showed that the temperature of fusion was, however, only lowered 2·8° for one hundred times the increase of surface (ten times decrease of radius). This therefore is probably a factor of no great magnitude.

Tammann (*Ann. Phys. Chem.*, 1899, [ii], **68**, 553, 629) showed that simple pressure was capable of influencing the melting and transition points of a large number of substances. He also showed (*Zeitsch. physikal. Chem.*, 1903, **46**, 818) that the fusion curve for sodium sulphate rose to a maximum at a pressure of 750 kilos. per sq. cm., and then fell considerably.

Most inorganic salts, however, have their fusion points raised by increase of pressure, and even in cases of the reverse, such as that of silver bromide, it is necessary to apply pressures of the order of 10^5 atmospheres to cause fusion at ordinary temperatures. Although the experimental facts do not yet seem to offer a complete explanation of the action of shearing stress as applied to solid substances, it thus appears probable that such stress has a peculiar action of its own towards the production on the surface of such materials of a state analogous to, if not identical with, fusion.

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XXXV.—*The Association of Organic Compounds in Benzene and Alcohol Solution as Determined by the Vapour Pressure Method.*

By William Ross Innes.

In a previous paper (T., 1902, **81**, 682), the author has described the results obtained in an investigation on the influence of temperature on association in benzene solution by Raoult's ebullioscopic method.

The investigation was undertaken chiefly with the view of discovering the cause of the very different behaviour of the acids and oximes on the one hand, and the anilides, alcohols, and phenols on the other, in hydrocarbon and other solvents, generally spoken of as associating solvents.

It seemed probable that if the different behaviour of these two classes of compound could be explained, some light would be thrown on the nature of association.

As is well known, the acids and oximes give data in dilute solution which indicate that the molecular weight is normal at extreme dilution; with increasing concentration, the value for the molecular weight rises, at first rapidly, then more slowly, until it reaches double the normal value; further increase of concentration affects the value but little in most cases.

Anilides, alcohols, and phenols behave quite differently, the molecular weight increasing, generally, almost linearly, and there is no indication of the molecular weight reaching a limit, even at the highest concentrations at which it is usual to carry out determinations by the cryoscopic and ebullioscopic methods.

The investigation failed in its main objective, and it was evident that more concentrated solutions would have to be examined in order to arrive at the desired result.

The reverse problem, namely, the behaviour of substances belonging to "the associating group of solvents" in alcohol, also seemed worthy of investigation.

It was decided to use the vapour-pressure method in this investigation. If the experimental results obtained by Raoult in ethereal solution by the vapour-pressure method are plotted to show molecular weight against concentration, the regularity of the curves, apart from the determinations in dilute solution, suggests that the statical method used is much more accurate than references to it in literature would lead one to suppose, and that little is needed to make it a satisfactory one.

It was originally intended to use the statical method. With Ramsay and Young's apparatus (*Phil. Trans.*, 1887, **178**, 57), the temperature could be varied over a wide range, and it was hoped, by boiling out the tube and stirring the solution, so as to prevent varying concentration at the free surface by evaporation or condensation of the solvent, that accurate results would be obtained. While the pressure apparatus was being made, the experiments described in the following pages were commenced, and the method gave such satisfactory results that it was continued until other work prevented the completion of the investigation.

The apparatus employed was essentially the same as that used in the ebullioscopic method (T., 1902, **81**, 685), except that the jacket of the boiling tube was not connected to the constant pressure apparatus, but to a separate reservoir with manometer and pump, so that the temperature of the jacket could be kept approximately at the temperature employed. A temperature about 3° higher than that of the boiling tube was aimed at. For the experiments at 75°, alcohol boiling under atmospheric pressure was used. The tube *L* of the regulator was graduated, so that the apparatus could be set to give the pressure required, and was fitted with a micrometer screw allowing of ready adjustment to 0·1 mm. or less. A barometer, trapped to prevent entrance of air to the upper part, stood in the same trough as the manometer *H*, and the difference in height was read on a millimetre mirror scale. This difference is, of course, the pressure in the apparatus, and is independent of the atmospheric pressure. A set of thermometers reading to 0·1° with open scale, made by Hicks, was used. They were not calibrated, as they were employed merely as zero instruments. That they were accurate and that the zero altered very little is shown by the vapour pressures obtained for benzene and alcohol at different temperatures. The exact temperatures are, of course, given by the vapour pressure of the solvent. In order to prevent changes of pressure affecting the volume of the thermometer bulb, the thermometer was placed in a tube fitting it closely and containing enough mercury to cover the bulb.

The boiling tube was of such size that from about 15 to 50 grams of solution could be used. It was of lead glass, and no platinum was fused through the bottom. It was packed with beads and platinum clippings, as already described (T., 1901, **79**, 262). The end of the condenser of the boiling tube was connected to a tube dipping into a fractionating flask to act as a trap in case of sudden frothing, and the side-tube of the fractionating flask passed into a drying tube which joined on to the constant-pressure apparatus. In order to obtain satisfactory results, it was found necessary to

take every possible precaution to exclude traces of moisture from the apparatus and chemicals.

The benzene used contained a trace of thiophen, it was of perfectly constant boiling point, and was dried over phosphoric oxide. The alcohol was finally dried with phosphoric oxide and distilled. It was of constant boiling point. The benzene and alcohol were kept in bottles, through the corks of which pipettes passed, the upper end of the pipette passing into a drying tube. The solvent was measured out in all cases.

Most of the substances were bought in a sufficient state of purity for use; a few were further purified. The dimethyl tartrate and β-benzilmonoxime were prepared. The substances were in most cases melted and cast in a glass tube. When solid, the tube was heated and the rod of substance pressed out. β-Benzilmonoxime could not be satisfactorily treated in this way and did not form pastilles readily; it was partly melted, allowed to cool, and broken into pieces of suitable size. The substances were prepared for use a day in advance and kept in a vacuum over sulphuric acid until required.

Method.

The boiling tube containing the solvent is connected to the constant-pressure apparatus, the regulator set to give approximately the pressure required, and the apparatus exhausted. When the pressure has fallen and the regulator begins to act, the gas is lit and adjusted to such a height that the benzene boils briskly. It is essential that boiling should be fairly rapid, otherwise in concentrated solutions layers of different concentration form and cause very large errors. After the solvent has been boiling for a few minutes, the regulator is altered until the temperature is that required ($t°$), and the apparatus left for an hour; if necessary, a further adjustment is then made, the barometer and manometer are read, and boiling is continued for a further ten minutes. If temperature and pressure are both constant, the first addition of solute is introduced in the manner already described (*loc. cit.*), the regulator being altered so as to lower the pressure by the amount which it is expected the vapour pressure will be lowered. When solution is complete, the pressure is altered until the temperature ($t°$) is again obtained, and the solution allowed to boil for ten minutes; a further adjustment is made if necessary, and the solution allowed to boil for a further ten minutes until constancy is obtained; the pressure is then read. Additions are then made under similar conditions until the concentration is about 50 per cent.

Beyond 50 per cent., very large additions have to be made to increase the concentration in the steps required. A fresh series was then started with 10 c.c. of solvent. The pressure of the solvent was determined as before, sufficient solute added to give a concentration of 50—60 per cent., and the additions continued as before up to 80 per cent.

In some cases, where only one series was carried out at a given temperature, 15 c.c. of benzene were used, and, after determining the vapour pressure, sufficient solute was added to cover completely the thermometer bulb. A range of concentration from about 15 to 70—80 per cent. was thus attained in one series. Beyond 80 per cent., determinations were made by weighing into the boiling tube a suitable amount of solute, a small amount of benzene was added, and the vapour pressure determined after the temperature had become constant; further additions of benzene were then made. In order to do this, the clip *p* was closed, the flame under the boiling tube removed, and the addition of benzene made with a long pipette. Before reopening the clip *p*, the pressure in the apparatus is increased considerably by opening the cock *e*, otherwise frothing would occur, and the clip is opened gradually to avoid loss of benzene vapour as much as possible. The regulator is moved to give a higher pressure, and the flame put back. At 75°, the pressure was allowed to become equal to the atmospheric. In this way, it was possible to work from a concentration of 95 per cent. downwards. At the highest concentration, a constant temperature was not attained. With azobenzene there was a very slow variation of a few tenths of a degree about a mean position. The determination took a very long time, owing to the extreme slowness of the temperature change. The method is not a practical one at a concentration of 95 per cent.; at 90 per cent., however, the difficulty almost entirely disappears with azobenzene as solute. Only two substances were examined at these concentrations, namely, the "normal" azobenzene and the very abnormal dimethyl tartrate. The determinations with dimethyl tartrate at these great concentrations were much more difficult than with azobenzene, especially in the determinations above 60 per cent. molecular concentration at 75°. The only method by which determinations could be made was to follow the change of temperature with corresponding change of pressure until the temperature remained constant for a time. In this way, a higher and lower limit of the vapour pressure was obtained. Owing to the slowness with which the temperature altered and the variation in the limit, it was not practicable to take a mean. The largest pressure, that is, the pressure corresponding with the highest molecular weight, was

taken in each case. Although the possible error in these determinations is large and not much value can be attached to the individual values, it seems fair to assume that the real molecular weights are not greater than those calculated.

At 53°, the temperature variation was much less than at 75°, and single determinations were carried out instead of series, so that the variations could be observed over sufficient time to take a mean. Even under these conditions, the experimental error appears to be large, the two determinations at nearly the same concentration showing a large difference in molecular weight.

In the determination at 63°, the temperature remained almost constant throughout the time ordinarily devoted to a series.

There seems little doubt that the variation of temperature in these experiments is due to the difficulty with which the benzene, returned from the condenser, mixed with the highly viscous solution, whilst the greater constancy at the lower temperatures may be due partly to the more efficient stirring of the larger bubbles of vapour formed at the lower pressure and partly to the smaller amount of benzene vapour condensed for similar rates of boiling.

Results.

The results obtained are given in tabular form on p. 430 ***et seq.***

Col. I. gives the temperature at which the series was carried out, as indicated by the thermometer $= t$.

II., the observed pressure of the solvent, no corrections being made $= p$.

III. $p - p'$, also without any correction.

IV., weight of solvent actually taken $= G$.

V., weight of solute $= g$.

VI., grams of substance per 100 grams of solution

VII., the percentage molecular concentration, $100n/n + N$.

VIII., the molecular weight found $= m'$.

IX., the association factor m'/m.

In calculating VI., VII., VIII., 0·4 gram is subtracted from the weight of the solvent in the experiments at the higher pressures and 0·3 gram in those at the lower pressures, to allow for the amount of solvent in the state of vapour and that wetting the walls of the tube above the solution.

The vapour-pressure method offers the advantage that a series of determinations at different concentrations can be carried out isothermally, whilst the great simplicity of the vapour pressure law for concentrated solutions of "normal" substances suggests that it will be easier to interpret the experimental results obtained

with more complex systems, where present-day theory offers little guide, than would be the case by the cryoscopic, ebullioscopic, or osmotic methods.

The vapour pressure law was first established experimentally by Raoult for non-volatile solutes in a volatile solvent, and was shown by him to apply satisfactorily for a number of solutes in ethereal solution even up to 80—90 per cent. concentration. It is, however, from the study of mixtures in which both constituents are volatile that the accuracy of the law has been experimentally established. It has been shown that for mixtures of non-associated, closely related liquids, the so-called ideal solutions, the law holds with great accuracy and within the limit of experimental error throughout the whole range of concentration from 0—100 per cent.

Raoult's law $\frac{p-p'}{p} = \frac{n}{N+n}$ is readily transformed algebraically into (2) $\frac{p-p'}{p'} = \frac{n}{n}$ and (3) $p' = p\frac{N}{N+n}$, on the assumption that n has the same value in both numerator and denominator, the last form being that most convenient for considering solutions in which both constituents are volatile, whilst (2) is a convenient form for calculating the results obtained with non-volatile solutes.

Where both constituents are volatile, it is evident that the distinction between solute and solvent entirely disappears, since for each constituent its partial pressure is proportional to the product of its pressure in the pure state and its molar fraction in the solution. The same must be true where the vapour pressure of one of the constituents of the solution is negligibly small, since this is merely a limiting case of the more general relation. It is therefore purely arbitrary which constituent we call solvent and which solute. In this communication, that constituent which separates in the pure state—as vapour in the vapour-pressure and ebullioscopic methods, as ice in the cryoscopic method—is referred to as the solvent, whatever its concentration in the solution.

The vapour pressure law has been deduced thermodynamically by several methods for two classes of solutions, namely, ideal solutions of any concentration and infinitely dilute solutions.

In deducing the law for ideal solutions, one of the simplifying assumptions that has to be made is that the constituents of the solution are not associated as pure liquids, and that no association takes place on mixing them. It is evident that the law thus derived becomes purely empirical when applied to associated solutions. That such an assumption has to be made does not show that the vapour pressure law is not applicable where association is

present; the assumption is merely a mathematical convenience. It seems reasonable to assume, for purposes of investigation and in absence of any evidence to the contrary, that if all the more chemical factors, association, ionisation, and solvation, are allowed for, the law will hold for any solution, and that the physical quantities which enter into the thermodynamic equation will be allowed for automatically, since these quantities are undoubtedly functions of the more chemical factors.

Although it is not at present possible to deduce the general laws for lowering of vapour pressure and freezing point, raising of boiling point, etc., we know that these laws are interconnected by a series of rigid thermodynamic differential equations which are independent of concentration, ionisation, association, and solvation, and can therefore be certain that general qualitative conclusions drawn from results obtained by one of these methods can be applied in discussing the results of any of the other methods, whether association, solvation, etc., occur or not.

The vapour pressure law can be deduced for dilute solutions without making any assumption as to the molecular aggregation of either solute or solvent, or as to whether solvation occurs. The only assumption necessary for thermodynamic treatment in this case is that the solution is infinitely dilute.

This method of derivation gives no information as to whether the law applies where association of the solute occurs, since we know as the result of a very large number of experimental determinations that zero association is always indicated at infinite dilution.

As regards solvation, it follows that where this occurs, the solvated complex behaves as a single molecule at infinite dilution, and it is reasonable to assume that in more concentrated solution the law is observed if the quantity of solvent solvated at a given concentration is subtracted from the total solvent.

It also follows from the method of deriving the law for dilute solutions, that in the vapour pressure relation $\frac{p-p'}{p} = \frac{n}{N+n}$. N, the number of molecules of the solvent, is that corresponding with the normal molecular weight, whatever degree of association the solvent may have in the liquid state.

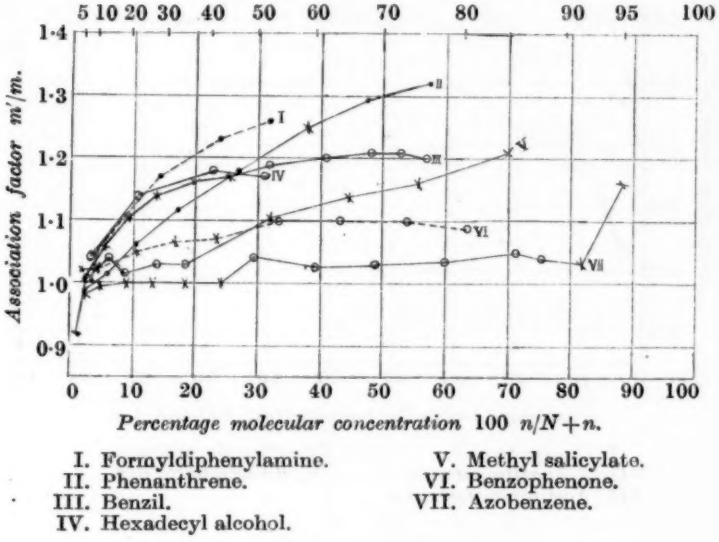
The evidence that the solution laws hold when association takes place is at present purely experimental, and rests on the formation of definite complexes by organic acids and oximes in a number of solvents. In the present communication, it is shown that formanilide and acetanilide also form definite complexes.

Benzene as Solvent.

The results obtained with a number of substances which did not show a great departure from Raoult's law are shown graphically in Fig. 1. Determinations belonging to different series on a curve are distinguished by circles, crosses, or dots.

It will be seen that there is a break in several of the curves where the series at lowest concentrations (5—50 per cent.) meets the next series (60—80 per cent.), and is naturally most marked where the curve is approximately straight. The break is obviously due to some form of experimental error in the second series,

FIG. 1.



I. Formyldiphenylamine.
II. Phenanthrene.
III. Benzil.
IV. Hexadecyl alcohol.
V. Methyl salicylate.
VI. Benzophenone.
VII. Azobenzene.

amounting sometimes to from 3 to 4 per cent., and apparently constant throughout the series. The cause of this error is not at all obvious.

One of the substances, azobenzene, obeys Raoult's law absolutely within the limit of experimental error.

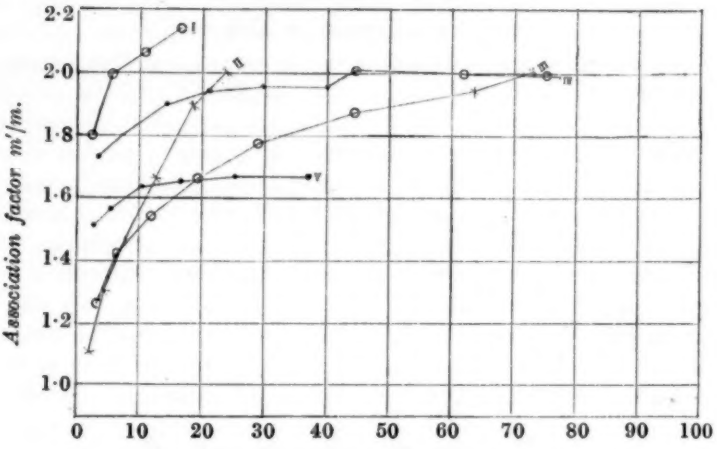
All the other substances show more or less association in concentrated solution. From the degree of their abnormality, the general conclusion may be drawn that those groups which cause slight but distinct association in dilute solution of the compounds of lowest molecular weight containing them, also cause a slight association in concentrated solution with compounds of such high

molecular weight that they do not show appreciable association in dilute solution, and, further, that the laws which connect the constitution of the solute with degree of association for the larger abnormalities in dilute solution also apply to the smaller abnormalities in concentrated solution.

Phenanthrene shows slight abnormality by both the cryoscopic and ebullioscopic methods; it is not therefore surprising that it shows distinct association in concentrated solution. The abnormality is, however, of interest, as on general grounds

FIG. 2.

Acids and oximes in benzene at 75°.



Percentage molecular concentration 100 $n/N+n$.

I. Cinnamic acid.
II. β-Benzilmonoxime.
III. Acetophenoneoxime.
IV. Phenylacetic acid.
V. *d*-Camphoroxime.

phenanthrene might be expected to form an ideal solution with benzene.

Acids and Oximes.

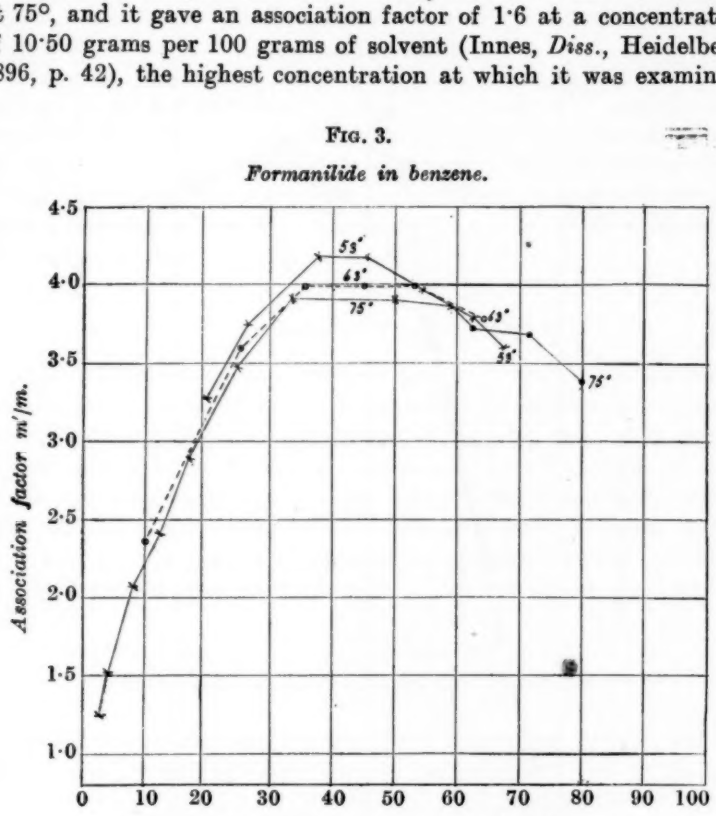
β-Benzilmonoxime, acetophenoneoxime, and phenylacetic acid all show a maximum association factor of 2. β-Benzilmonoxime was not sufficiently soluble to carry the series further (Fig. 2).

Cinnamic acid shows a decided tendency to give a higher molecular weight than that corresponding with the double formula; it seems probable that this is due to the presence of a double bond in the molecule. The solubility was not sufficient to carry the series further. *d*-Camphoroxime shows a rapid increase in associa-

tion up to 10 per cent., but only reaches a maximum of 1·66, and has almost this value over a range of 27 per cent. By the cryoscopic method in benzene, association factors approaching 2 are obtained even in 5 per cent. solution. In naphthalene (m. p. 80°), on the other hand, its behaviour is very similar to that in benzene at 75°, and it gave an association factor of 1·6 at a concentration of 10·50 grams per 100 grams of solvent (Innes, *Diss.*, Heidelberg, 1896, p. 42), the highest concentration at which it was examined.

FIG. 3.

Formanilide in benzene.



The low maximum would therefore seem to be connected with the temperature at which the determinations were carried out.

Anilides.

The results obtained with formanilide are shown graphically in Fig. 3.

Series of determinations were made at 75°, 63°, and 53°.

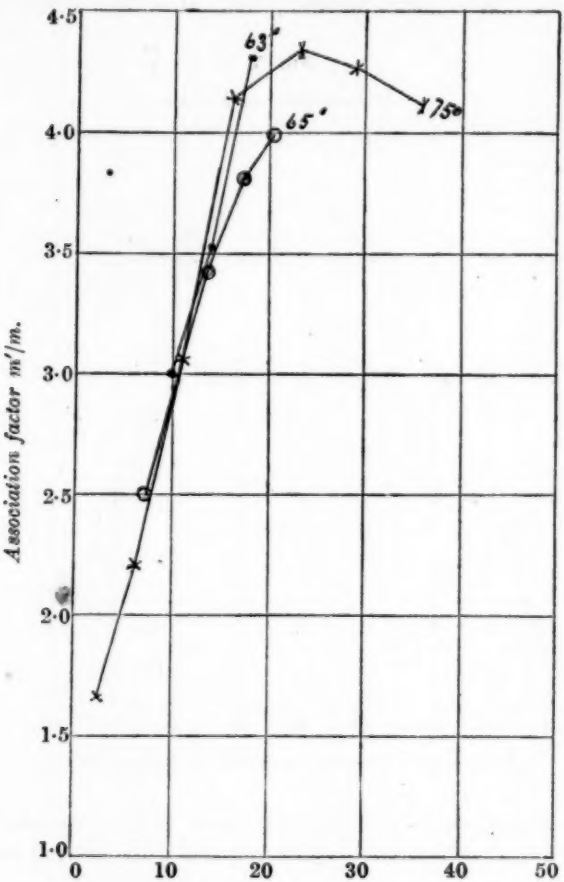
The constancy of the association factor over a considerable range of concentration at 75° and 63°, as well as the small temperature

effect on the maximum, points to the formation of a definite molecular complex containing four simple molecules.

Acetanilide gives a curve at 75° similar to that of formanilide, but the rate of association is still more rapid (Fig. 4).

FIG. 4.

Acetanilide in benzene.



At 63° the solubility is considerably less than at 75°; at both temperatures, the solution of highest concentration is nearly saturated. The series at 63° was repeated at 65°, as a doubt was felt as to whether the whole of the solute was in solution in the last determination at 63°. With the exception of this determina-

tion, the curves at 63° and 65° are either practically identical with that at 75° or below it, indicating an increase of association with increase of temperature.

Since increase of association with increase of temperature is improbable, and the values at 63° and 65° fall well on the same curve, it seems possible that the series at 75° is affected by experimental error.

Taken by themselves, the values obtained with acetanilide do not point to the formation of a definite molecular complex, but the fact that there is not more difference in the maximum values of acetanilide and formanilide, although the concentrations at which they reach this maximum are so different, does indicate that such a complex is formed. There seems to be a slight tendency to further association, as with formanilide at 53°.

Dimethyl Tartrate.

This substance, containing two hydroxyl groups, is extremely abnormal. Its behaviour in dilute solution at different temperatures has already been investigated (Innes, *loc. cit.*). In concentrated solutions, it shows the characteristic alcohol type of curve up to concentrations approaching 50 per cent. molecular, and the influence of temperature both on the rate of increase of association and on the maximum association is most striking. There is no evidence of the formation of a definite molecular complex (Fig. 5).

The values obtained beyond equimolecular concentration at 63° and 53° suggest that the molecular weight would be normal at 100 per cent., and that the shapes of the upward and downward curves on each side of equimolecular concentration are either identical (apart from experimental error) or very similar. Lines of equal slope are shown dotted in the figure. The values obtained at 75° are not consistent with this being the case, but, as has already been pointed out, the probable error in these series, at high concentrations, is much greater than at the lower temperatures.

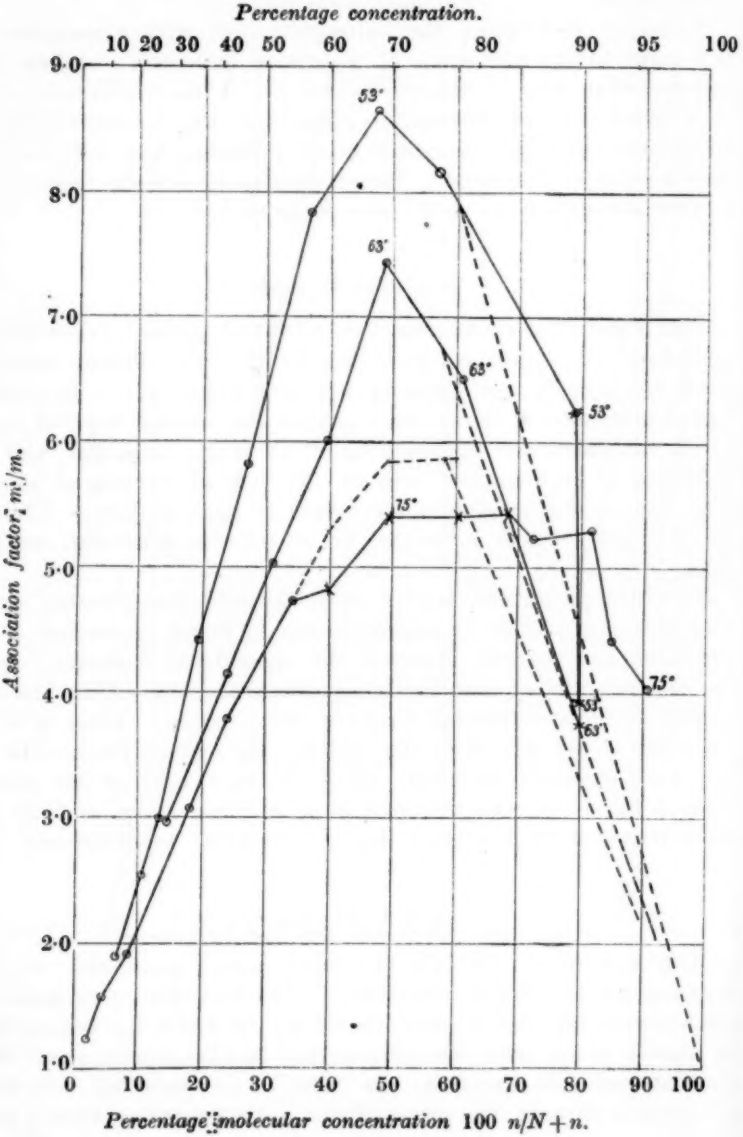
Ethyl p-*Hydroxybenzoate.*

This substance, the only abnormal phenol examined, was unfortunately of limited solubility. The first two determinations show a very rapid increase of association, and the line joining them is almost linear with the intersection of the co-ordinates. With increase of concentration, the rate of increase of association diminishes rapidly, the shape of the curve indicating that a maxi-

mum would be reached with an association factor between 2·8 and 3. As the solubility would be less at lower temperatures, it seemed useless further to examine this substance.

FIG. 5.

Dimethyl tartrate in benzene.



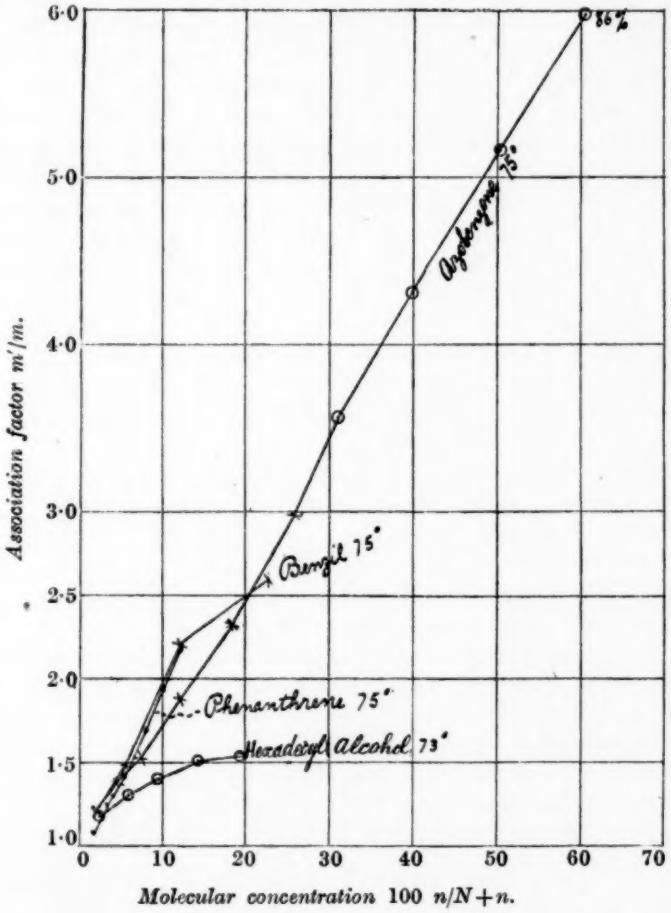
Alcohol as Solvent.

Four substances were examined in alcohol, and all were found to give abnormal molecular weights (Fig. 6).

Phenanthrene and benzil give practically identical molecular

FIG. 6.

Alcohol as solvent.



weights at equal molecular concentrations up to the limit of solubility of phenanthrene, and the rate of increase is nearly linear and very rapid. The last determination with benzil shows a decreasing rate of association.

Azobenzene is also extremely abnormal; it gives values for the molecular weight somewhat smaller than those with benzil and phenanthrene at the same molecular concentration, and the rate of increase is at first slightly less, then slightly greater, than linear. The last four determinations (63·2 to 85·9 per cent.) are exactly linear, and when produced to zero concentration, give the normal molecular weight with considerable accuracy.

Hexadecyl alcohol is about twice as abnormal as in benzene.

The view is very generally held that organic solutes should show less tendency to association in alcohol than in benzene, since the conductivity of electrolytes in benzene is extremely small, whilst in alcohol their conductivity is considerable, and it has been assumed that a substance with dissociating power for electrolytes would not favour the formation of complex molecules. If we admit this view, it might be argued that the abnormalities in alcoholic solution are not due to association. The fact that three substances of such different constitution as azobenzene, phenanthrene, and benzil should all be highly abnormal and to almost the same extent over a considerable range of concentration, whilst in benzene, in concentrated solution, they behave so differently, also suggests that the abnormality is not due to the solute, *per se*, but to some specific action of the solvent. It therefore seems advisable to consider the possible ways in which the solvent could exert an influence on the apparent molecular weight.

That associated liquids, such as alcohol, have an abnormally low vapour pressure has been well established (Vernon, *Chem. News*, 1891, **64**, 54; Young, *Phil. Mag.*, 1892, [v], **34**, 507; T., 1893, **63**, 1251; van't Hoff, "Lectures," Part 3, 50). It is also known that, in solution, alcohol is non-associated at sufficient dilution, whether in an inert or in an associating solvent.

If, therefore, we add to alcohol a miscible, inert, non-volatile liquid, the vapour pressure of the alcohol will not be that corresponding with its molar fraction, but will be larger by an amount which is a function of the dissociation of the complex molecules of the alcohol. An abnormally small lowering of the vapour pressure will therefore be obtained. The effect of the smaller lowering of the vapour pressure will be to increase p' and decrease $p-p'$ in $m=\frac{gMp'}{G(p-p')}$, and both these influences will increase the apparent molecular weight. With such an inert solute, in a solvent the liquid molecules of which are associated, but not the vapour molecules, we should expect to get values for the molecular weight of the solute, which point to the normal molecular weight at extreme dilution, and increase with concentration at a rate which is a

function of the dissociation of the complex molecules of the solvent. Hexadecyl alcohol might be expected to be such an inert solute with respect to alcohol, since it appears to be a general rule that substances of constitution similar to that of the solvent give normal molecular weights in that solvent. The departure of hexadecyl alcohol from Raoult's law may therefore be attributed to the progressive dissociation of the alcohol as it is diluted with the hexadecyl alcohol, and the much greater abnormality of the other substances must be sought in some other influence.

When there is combination between the solute and solvent, it is evident that part of the solvent is removed from the solution and no longer functions as solvent. G is therefore decreased, and at the same time p' will be decreased owing to the increased concentration of the solute complex, and $p-p'$ increased. The decrease of G and p' and the increase of $p-p'$ would all act in the direction of decreasing the molecular weight. It is further evident that the influence of such combination will become very great as the concentration approaches $n=N$, provided the compound or complex formed does not exert a decided vapour pressure.

After the experiments described in this paper had been carried out, the apparatus was used by Mr. B. C. Burt, who determined the vapour pressure of concentrated sulphuric acid solutions (T., 1904, **85**, 1345). His results, when suitably plotted (Fig. 7), show in a most striking manner the influence of combination between solute and solvent in molecular weight determinations in concentrated solutions.

Burt determined the vapour pressure of solutions ranging from 25 to 95 per cent., and calculated the molecular weights by Raoult's formula, using Regnault's values for the vapour pressure of water. The experimental figures at 100° were used when available; at the higher concentrations, it was necessary to take results at higher temperatures. As the influence of temperature at these high concentrations is very small, the form of the curve cannot be seriously affected. The curve of molecular weight against percentage concentration shows the influence of $n=N$ most clearly. There is first a rapid, then a slower fall until $n=N$ is reached, after which the molecular weight is practically constant and almost zero.

Since, in a solution in which the solute is practically non-volatile and the solvent readily volatile, any chemical compound formed must have a much smaller vapour pressure than that of the solvent, it is evident that, in such solution, combination between solvent and solute cannot occur if the normal or a high molecular weight is indicated at or near equimolecular concentration.

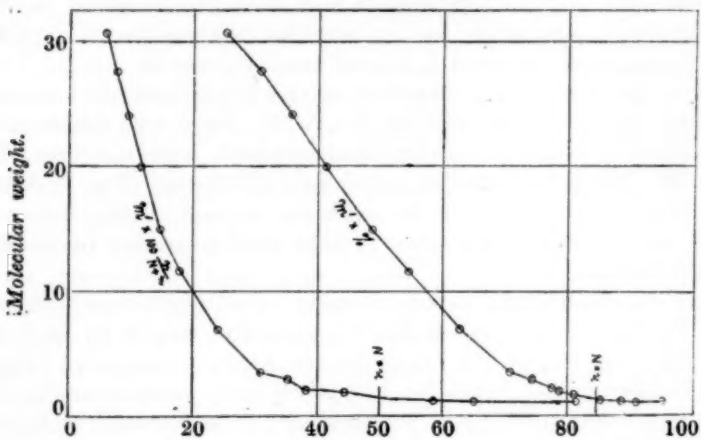
Since neither the dissociation of the solvent nor combination

between solute and solvent will explain the great abnormality of phenanthrene, benzophenone, and azobenzene in alcohol, it can only be supposed that the abnormality is due to association, and it follows *that alcohols and the "associating solvents" exert an associating influence on each other.*

Alcohol was first used as an ebullioscopic solvent by Beckmann (*Zeitsch. physikal. Chem.*, 1890, **6**, 454), and from his results in this and other solvents, he drew the conclusion that solvents like the alcohols, organic acids, and phenols, containing hydroxyl groups, are "dissociating solvents of the water type," and consequently complex molecules are not formed in them. Nernst lent support to Beckmann's hypothesis, by the theory that the higher

FIG. 7.

Apparent molecular weight of sulphuric acid (1) *against molecular concentration,* (2) *against percentage concentration.*



the dielectric constant of a solvent, the greater will be its power to split up double molecules.

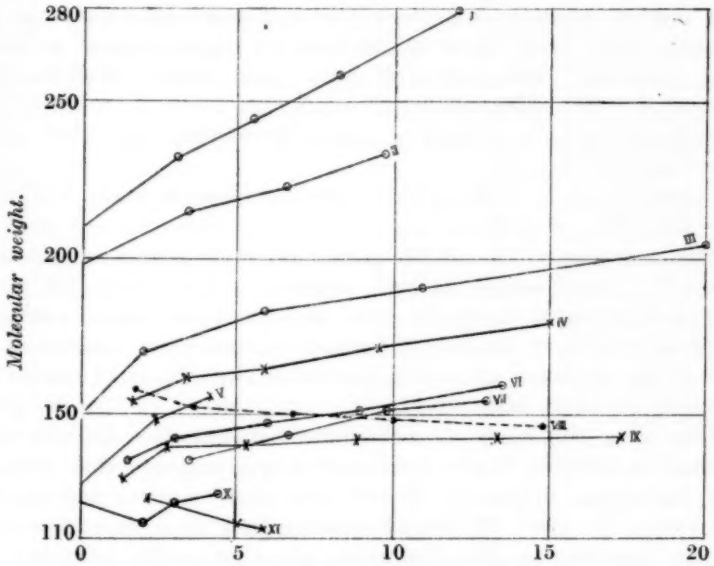
It is of interest to examine the experimental results on which Beckmann founded his theory. These are shown graphically in Fig. 8 for alcoholic solutions, molecular weights being plotted against concentration. Carbamide and racemic acid have not been included, the former because it was only examined in dilute solution, the latter because the values are irregular.

A glance at the curves will show that, with the exception of the acids, all the substances show a much more rapid increase of molecular weight than is shown by "normal" substances in benzene or naphthalene. Benzil, phenyl benzoate, ethyl benzoate,

and naphthalene, substances belonging to the "associating type" of solvent, are very abnormal; borneol, acetophenoneoxime, and acetanilide, belonging to the "water type," are less abnormal, and the curves of the last three substances are approximately parallel. If the view already brought forward, that the abnormality of hydroxy-compounds in alcohol is due to the dissociation of the

FIG. 8.

Beckmann's results in alcohol by the ebullioscopic method.



Grams of solute per 100 *grams of solvent.*

I. Benzil, 210.
II. Phenyl benzoate, 198.
III. Ethyl benzoate, 150.
IV. Borneol, 154.
V. Naphthalene, 128.
VI. Acetanilide, 135.
VII. Acetophenoneoxime, 135.
VIII. Tartaric acid, 150.
IX. Salicylic acid, 138.
X. Benzoic acid, 122.
XI. Succinic acid, 118.

alcohol complex, is correct, these curves should be parallel for equal molecular concentrations.

Succinic and tartaric acids show a decreasing molecular weight with concentration; evidently this is due to ester formation and combination of the water formed with the solvent. The normal molecular weights with salicylic acid must be attributed to a balance between the abnormality due to the dissociation of the solvent and that due to ester formation.

Beckmann's results therefore lend strong support to the deduction that there is mutual association between alcohols and substances of the hydrocarbon type.

Beckmann's classification into two types is still useful, however, and it is proposed to call the "associating solvent" type of substance *Carbotype*, and the "water type" of substance *Oxytype*, without, however, assuming any sharp line of demarcation between the two classes.

Numerous instances have been published of the comparatively normal behaviour of hydroxylated compounds and anilides in ethyl and methyl alcohols, but very few instances of association in alcohol, apart from those in Beckmann's paper, appear to have been observed. The following have been found (Peddle and Turner, T., 1911, **109**, 696):

m-Dinitrobenzene, 2·6—5·5, 1/100 gram-mols, per 100 c.c., $m'=181$—211, $m=168$.

Diphenylamine, 3·79—5·99, 1/100 gram-mols. per 100 c.c., $m'=190$—206, $m=169$.

Phenanthrene, 1·94—11·99 grams per 100 grams of solvent, $m'=183$—226 (Behrend, *Zeitsch. physikal. Chem.*, 1892, **10**, 279).

Numerous salts, inorganic and organic, have been examined ebullioscopically in alcohol, and many of these show association as well as the influence of combination with the solvent (Turner and Pollard, T., 1914, **105**, 1751).

The close similarity in behaviour between the alcohols and phenols in solvents of the hydrocarbon type suggests that phenols and carbotype substances should also show mutual association. Robertson (T., 1906, **89**, 567) has shown that the hydrocarbons are highly associated in phenol solution, also that carbon tetrachloride is as abnormal as the hydrocarbons. Ethylene dibromide and bromoform are also abnormal, but to a less extent. The mutual association of the abnormal phenols and substances of the carbotype group must therefore be considered to be a general phenomenon.

The degree of abnormality of the substituted phenols follows definite laws as regards the nature and position of the substituting group, and the anilides follow similar laws. There seems little doubt, therefore, that a carbotype solute will give abnormal molecular weights in an anilide, and that mutual association takes place in this case also. Anilides do not seem to have been used as cryoscopic solvents, although formanilide (m. p. 46°) would be a convenient substance to use.

If mutual association takes place with acids and oximes in a carbotype solvent, it is obvious that no direct evidence of this

being the case can be obtained from the behaviour of a carbotype solute in an acid or oxime if the acid or oxime is associated to a double molecule in the liquid state.

There is, however, evidence that during the association of an acid or oxime in a carbotype solvent, the solvent exerts a specific influence on the association of a nature which has not been explained. If the solvent merely acted as a diluent, the mass law should apply to the dissociation of the double molecules, as in gaseous dissociation. Auwers (*Zeitsch. physikal. Chem.*, 1907, **60**, 385) has shown that with acids and oximes this is by no means the case, C_1^2/C decreasing very rapidly with concentration.

The data obtained in the present investigation are more suitable for such calculations than those used by Auwers, since the determinations were made isothermally; the results of calculation are, however, similar. The anilides also show large variations in the value of C_1^4/C.

Since there is direct and fairly conclusive evidence of mutual association between alcohols and phenols and a carbotype, it is reasonable to ascribe the influence of the carbotype solvent on the association of the acids, oximes, and anilides to the same cause.

The position of the maximum association of dimethyl tartrate in benzene at or near equimolecular concentration evidently indicates that in this instance association of solute and solvent takes place at the same rate. Although there is no evidence as to the rate of association of the solvent in other instances, it is not unreasonable to assume, for purposes of further investigation, that in a solvent which is non-associated in the liquid state, association of solvent and solute is in general equal.

The cause of mutual association of solute and solvent obviously cannot be chemical, as anything in the nature of combination between the two constituents, in concentrated solution, is impossible (p. 425). The only adequate explanation which has occurred to the author is that it is electrical in character.* It seems reasonable to suppose that the association begins in the oxytype substance, whether this is functioning as solvent or solute. If we imagine that for each molecule entering into an aggregate a definite quantity of electricity passes to the carbotype substance, causing in it an association equal to that in the oxytype, and that this goes on until an equilibrium is attained, depending on the temperature, concentration, pressure, and nature of the solvent and solute, this would account for the fact that dimethyl tartrate and benzene appear to associate at the same rate.

* That association may be due to electrical, not chemical, forces has already been suggested by Turner and English (T., 1914, **105**, 1793).

If we assume that the charge that passes when a substance associates is one electron per molecule, the charge per aggregate must be considerable when the association reaches 6—10, as with dimethyl tartrate. It might therefore be supposed that the molecules would arrange themselves in a definite geometric arrangement depending on their mutual attractions and repulsions, and that they would resist any influence which tended to alter this arrangement. The high viscosity of associated solutions would thus be explained.

Benzene as Solvent.

Azobenzene, $C_{12}H_{10}N_2=182$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'	m'/m.
75°	64·98	1·69	17·8	1·059	5·72	2·54	178	0·978
		3·34		2·193	11·2	5·12	181	0·995
		6·05		4·185	19·3	9·28	182·5	1·002
		8·72		6·30	26·6	13·3	182·5	1·002
		11·98		9·19	34·55	18·5	182	1·000
		15·78		13·02	42·9	24·2	182	1·000
75	65·09	18·89	8·9	8·54	49·7	29·8	189	1·042
		25·12		12·98	60·1	39·3	187	1·026
		31·30		19·18	69·0	49·0	188	1·030
		38·19		29·52	77·4	59·6	188	1·035
		45·69		49·56	85·2	71·3	191	1·050
		48·49		60·78	87·6	75·2	189	1·039
75	65·10	56·94	2·66	44·72	95·0	88·2	212	1·16
		53·3	4·435		91·8	82·1	187	1·03
		48·15	7·10		88·6	73·5	181	0·995

Benzophenone, $C_{13}H_{10}O=182$.

72°	58·84	1·27	22·19	1·144	4·98	2·20	185·5	1·02
		3·62		3·422	13·56	4·54	186	1·02
		6·23		6·321	22·4	11·03	191	1·05
		9·49		10·42	32·3	17·0	194	1·065
		12·95		15·52	41·7	23·4	195	1·07
75	65·18	20·27	8·90	9·98	53·6	33·3	200	1·10
		26·55		15·17	63·7	43·1	200	1·10
		33·36		23·25	73·0	53·9	201	1·10
		40·07		34·95	80·4	63·5	198	1·09

Benzil, $C_{14}H_{10}O_2=210$.

75	65·02	0·59	22·19	0·567	2·53	0·955	202	0·92
		1·72		1·622	6·94	2·68	213	1·013
		3·46		3·517	13·9	5·65	224	1·067
		5·68		6·18	22·0	9·52	232	1·105
		8·04		9·38	30·0	13·7	239	1·140
		11·35		14·43	40·9	20·1	244	1·16
		14·80		20·27	48·2	25·6	246	1·17
75	65·17	18·53	8·90	10·94	56·1	32·0	250	1·19
		23·85		16·06	65·2	41·0	252	1·20
		28·22		21·42	69·2	48·1	254	1·21
		31·57		26·32	75·2	53·1	254	1·21
		34·27		30·88	78·3	57·1	522	1·20

Benzene as Solvent—(continued).

Formyldiphenylamine, $C_{13}H_{11}ON = 197$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m
75	65·21	1·46	17·8	1·015	5·51	2·26	198	1·005
		2·72		2·017	10·40	4·39	208	1·05
		5·21		4·229	19·6	8·81	218	1·105
		8·35		7·562	30·2	14·73	230·5	1·17
		12·41		12·69	42·1	24·25	242	1·23
		17·76		20·79	54·5	32·2	249	1·26

Methyl Salicylate, $C_8H_8O_3 = 152$.

75	64·90	1·71	22·19	1·176	5·10	2·69	153	1·005
		4·05		2·944	11·92	6·49	158	1·04
		5·65		4·171	16·06	8·94	155	1·015
		8·81		6·871	23·9	13·9	156·5	1·03
		11·70		9·822	31·05	18·7	160	1·05
75	65·18	42·85	4·45	18·83	82·1	70·0	185	1·21
		33·81	8·01		71·1	55·6	177	1·16
		26·89	12·46		60·9	44·4	174	1·14
		21·8	17·8		52·0	32·4	168	1·105

Phenanthrene, $C_{14}H_{10} = 178$.

75	65·13	1·74	22·19	1·340	5·80	2·62	175	0·984
		3·94		3·242	12·95	6·11	180·5	1·101
		6·62		6·002	21·6	10·8	189	1·060
		10·39		10·57	32·6	17·5	199	1·118
		15·61		18·63	46·2	27·2	211	1·18
75	65·14	21·18	8·90	11·82	58·0	37·8	223	1·25
		26·62		17·56	67·3	47·3	230	1·29
		32·98		26·59	73·5	57·6	235	1·32

Hexadecyl Alcohol, $C_{16}H_{34}O = 242$.

75	65·24	1·09	22·2	1·029	4·50	1·49	217	0·90
		2·04		2·261	9·40	3·24	251	1·04
		4·19		5·008	18·7	6·87	260	1·07
		6·34		8·30	27·6	10·92	276	1·14
		9·58		13·38	38·0	16·5	278	1·15
		13·24		20·245	47·1	23·0	285	1·18
		18·06		30·23	58·2	30·9	284	1·17

Cinnamic Acid, $C_9H_8O_2 = 148$.

75	64·94	1·07	17·8	0·999	5·73	2·94	263	1·78
		1·96		2·024	10·43	5·77	291	1·965
		3·66		4·074	18·95	11·0	306	2·06
		5·92		7·10	28·95	16·5]	316	2·14

Benzene as Solvent—(continued).

Phenylacetic Acid, $C_8H_8O_2=136$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m',	m'/m.
75	65·26	1·29	17·8	1·059	5·73	3·36	236	1·73
		2·62		2·274	11·54	6·95	244	1·79
		5·23		5·032	22·4	14·2	258	1·90
		7·94		8·13	31·8	21·1	263	1·935
		11·79		13·07	42·8	30·0	265	1·95
		16·57		20·08	53·6	39·8	265	1·95
75	65·51	18·56	8·9	12·06	58·5	44·8	280	2·06
		29·74		24·53	74·2	62·0	270	1·99
		40·23		44·86	84·0	75·2	259	1·90

Acetophenoneoxime, $C_8H_9ON=135$.

75	65·12	1·70	17·8	1·013	5·50	3·26	169·6	1·26
		3·09		2·127	10·91	6·60	192	1·42
		5·33		4·132	19·2	12·04	208	1·54
		8·19		7·174	29·2	19·25	224	1·66
		12·15		12·21	41·2	28·9	239	1·77
		19·43		23·92	57·9	44·4	252	1·87
75	65·20	37·5	4·43	19·31	82·4	72·9	269	1·99
		31·15	6·65		75·4	63·8	261	1·94

γ-*Benzilmonoxime*, $C_{14}H_{11}O_2N=225$; m. p. 113—114°.

75	65·30	1·16	17·8	1·046	5·69	2·03	259	1·15
		2·09		2·167	11·11	4·15	295	1·31
		3·62		4·36	20·0	8·00	333	1·475
		5·20		7·34	29·7	12·71	397	1·68
		7·13		11·63	40·1	18·72	425	1·89
		8·87		15·81	47·6	23·98	450	2·00

l-d-*Camphoroxime*, $C_{10}H_{17}ON=167$.

75	65·16	1·22	17·8	1·072	5·80	2·80	252	1·51
		2·29		2·125	10·90	5·40	261	1·56
		4·33		4·316	19·9	10·4	272	1·63
		6·96		7·375	29·7	16·5	276	1·65
		10·99		12·54	41·9	25·2	278	1·66
		17·33		21·96	55·6	37·2	272	1·625

Formanilide, $C_7H_7ON=121$.

75	65·20	1·21	22·19	0·795	3·51	2·28	150·5	1·245
		1·78		1·482	6·36	4·19	189	1·562
		2·73		3·014	12·12	8·19	247	2·04
		3·63		4·812	18·1	12·45	293	2·42
		4·28		6·897	24·0	16·93	353	2·91
		5·60		10·99	33·5	24·43	422	3·48
		7·41		17·03	43·9	33·4	475	3·93
		10·39		25·02	54·6	50·3	473	3·91
		14·10		35·99	62·3	58·9	466	3·86

Benzene as Solvent—(continued).

Formanilide, $C_7H_7ON = 121$—(continued).

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m.
75	65·14	11·71	8·90	10·98	56·1	45·1	454	3·74
		15·64		15·82	64·8	54·1	454	3·74
		19·88		21·92	71·8	62·3	250	3·72
		26·85		33·05	79·5	71·4	428	3·53
		35·23		53·23	86·3	80·0	410	3·38
63	43·53	1·87	13·3	2·137	14·1	9·58	288	2·36
		3·74		6·817	34·4	25·25	436	3·60
		5·33		11·14	46·3	35·5	479	3·96
		7·41		16·65	56·2	45·2	486	4·02
		9·70		22·75	63·7	52·9	476	3·94
		14·19		36·87	73·7	64·6	458	3·78
53	30·28	2·10	13·3	4·924	27·4	19·6	396	3·27
		2·62		7·130	35·4	26·1	451	3·74
		3·78		12·07	48·0	37·4	508	4·19
		5·07		16·92	56·6	45·6	505	4·18
		6·99		23·97	64·9	54·4	480	3·96
		9·27		33·65	72·2	62·7	458	3·79
		11·05		41·64	76·4	67·4	435	3·60

Acetanilide, $C_8H_9ON = 135$.

75	64·96	1·36	17·8	1·070	5·76	2·43	224	1·66
		1·83		1·931	10·0	6·03	299	2·21
		2·45		3·628	17·2	10·8	414	3·06
		2·86		5·79	24·9	16·1	563	4·17
		4·20		9·05	34·2	23·1	586	4·34
		5·73		12·45	41·7	29·2	576	4·26
		7·87		17·18	49·7	36·2	557	4·12
63	43·60	1·55	22·2	4·18	16·0	9·93	404	2·99
		1·94		6·23	22·2	14·1	480	3·55
		2·16		8·43	27·8	18·2	580	4·30
65	46·58	1·39	22·2	3·041	12·2	7·41	354	2·62
		2·04		5·895	21·2	13·40	461	3·42
		2·48		7·96	26·6	17·45	507	3·76
		2·92		9·95	31·2	20·6	532	3·95

Dimethyl Tartrate, $C_6H_{10}O_6 = 178$.

75	64·97	1·08	17·8	0·853	4·66	2·1	226	1·22
		1·97		1·829	9·54	4·62	262	1·47
		2·97		3·524	14·7	8·15	342	1·92
		3·69		5·94	25·4	13·03	441	2·48
		4·33		8·78	33·5	18·1	550	3·08
		4·99		12·59	41·9	24·0	677	3·80
		6·57		20·78	54·5	34·3	826	4·64
75	65·20	6·59	8·90	8·50	49·7	30·4	687	3·86
		7·82		12·92	60·0	39·8	860	4·82
		10·00		19·27	69·1	49·6	966	5·43
		14·3		29·89	77·6	60·5	966	5·42
		18·41		42·32	83·2	68·5	976	5·49

Benzene as Solvent—(continued).

Dimethyl Tartrate, $C_6H_{10}O_6=178$—(continued).

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m.
75	65·18	46·25	2·76	55·71	95·8	90·9	725	4·07
		36·67	4·54		92·9	85·2	796	4·47
		30·06	5·85		91·2	81·8	930	5·22
		20·83	9·70		85·8	72·4	995	5·60
63	43·63	2·56	13·3	5·443	29·5	15·5	524	2·94
		3·09		9·37	41·8	23·9	739	4·15
		3·56		13·22	50·5	30·8	895	5·02
		4·16		19·27	59·6	39·4	1099	6·17
		4·92		28·08	68·4	48·6	1324	7·44
		8·47		46·42	78·3	61·0	1155	6·50
[63	43·53	24·53	4·43	45·35	91·5	80·3	664	3·72
53	30·23	1·04	13·3	2·053	13·4	6·47	338	1·89
		1·31		3·416	20·8	10·3	452	2·54
		1·53		4·69	26·4	13·6	528	2·97
		1·56		7·14	35·4	19·3	788	4·42
		1·81		11·00	45·8	26·9	1038	5·83
		2·07		17·09	56·7	36·5	1395	7·84
		2·88		26·07	66·8	46·9	1540	8·66
		4·23		39·4	75·2	57·1	1453	8·16
53	30·2	11·4	6·65	54·46	89·6	79·1	1113	6·25
53	30·2	15·4	6·21	54·68	90·3	80·2	694	3·9

Ethyl p-*Hydroxybenzoate*, $C_9H_{10}O_3=166$.

75	65·16	1·18	17·8	0·900	4·91	2·38	219	1·32
		1·97		2·017	10·4	5·17	290	1·75
		3·21		4·299	19·8	10·4	372	2·24
		4·70		7·48	30·0	16·8	430	2·59
		7·10		12·47	41·7	25·2	455	2·74

Alcohol as Solvent.

Hexadecyl Alcohol, $C_{16}H_{24}O=242$.

73	61·90	1·39	15·78	2·114	12·1	2·54	276	1·14
		2·80		4·995	24·5	5·82	316	1·30
		4·23		8·25	34·8	9·26	347	1·43
		6·14		13·43	46·7	14·3	365	1·51
		8·43		19·60	56·0	19·5	372	1·54

Benzil, $C_{14}H_{10}O_2=210$.

75	66·85	0·54	19·72	0·893	4·41	0·98	261	1·24
		1·21		2·023	9·50	2·20	261	1·24
		2·57		5·352	21·6	5·61	316	1·505
		4·02		12·42	39·2	12·12	462	2·20
		5·38		20·01	50·9	22·4	544	2·59

Alcohol as Solvent—(continued).

Phenanthrene, $C_{14}H_{10}=178$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m.
75	66·91	1·10	15·78	1·105	6·70	1·82	198	1·11
		2·15		2·483	13·87	4·01	224	1·26
		3·00		4·399	22·2	6·89	279	1·57
		3·92		7·65	33·1	11·4	368	2·06
75	66·97	0·90	19·72	1·033	5·09	1·36	181	1·016
		1·19		1·462	7·03	1·92	190	1·07
		1·87		2·667	12·12	3·45	222	1·247
		2·75		4·537	19·06	5·71	252	1·42
		3·28		6·54	25·3	8·02	303	1·70
		3·59		8·192	29·8	9·88	344	1·93
		4·03		10·40	35·0	12·20	368	2·17

Azobenzene, $C_{12}H_{10}N_2=182$.

75	67·15	1·26	15·78	1·356	8·09	2·18	212	1·165
		2·36		2·881	15·8	4·52	236	1·30
		3·47		5·029	24·6	7·63	276	1·52
		4·56		8·30	35·0	12·0	342	1·88
		5·70		13·08	46·0	17·8	421	2·31
		6·88		20·60	57·2	25·3	550	2·96
75	67·15	7·35	7·89	12·95	63·2	30·4	647	3·56
		8·90		19·45	72·3	39·6	781	4·29
		10·98		29·84	80·1	50·2	939	5·16
		13·63		45·05	85·9	60·2	1083	5·96

The experiments described in this paper were made in the Chemical Laboratories of the University of Liverpool and the Harris Institute, Preston. The author wishes to express his indebtedness to the late Dr. J. C. Brown for supplying a dividing engine and several chemicals, and to Dr. P. F. Frankland for the loan of the electromagnetic stopcock.

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XXXVI.—*The State of Potassium Oleate and of Oleic Acid in Solution in Dry Alcohol.*

By MARY EVELYN LAING.

EVER since Krafft's second paper (Krafft, *Ber.*, 1899, **32**, 1584; compare Krafft and Strutz, *Ber.*, 1896, **29**, 1328) on the molecular weights of the salts of the higher fatty acids in dry alcohol, soap has served as the typical instance of a substance which is a crystal-

loid of normal molecular weight in alcohol, although in water it is a colloidal electrolyte.* This conception and definition of colloidal electrolytes to which the six years' study of soap solutions in this laboratory up to 1914 has led, made it appear possible that in alcohol also the apparent simplicity of Krafft's last result was illusory and that, as in some aqueous solutions, extensive dissociation and formation of colloid might occur, the more so since his previous paper had indicated that in absolute alcohol soap existed in the form of double molecules. For this reason, the molecular weight in alcohol has been redetermined. Further, the electrical conductivity has been measured in order to ascertain whether the ionisation is great or negligible.

Potassium oleate was chosen for study because of its ready solubility in alcohol, since in many cases the formation of colloid or colloidal electrolyte is only appreciable in high concentration. Its solutions are never devoid of opalescence, and they have a distinct tendency to froth.

The result has been to show that potassium oleate both in anhydrous and in moist ethyl alcohol is essentially a simple electrolyte dissociating to a very moderate extent into simple ions. Only quite small amounts of colloid can be present.

Solutions of oleic acid, which also froth readily and for which no ebullioscopic data existed, were likewise investigated, particularly as Dennhardt (*Diss.*, 1898; *Ann. Phys. Chem.*, 1899, [iii], **67**, 325) had obtained conducting curves in methyl and ethyl alcohols, exhibiting in each case a pronounced maximum and minimum. Such phenomena are of very frequent occurrence in the literature of non-aqueous solutions, and in certain cases their explanation appears to me to offer great difficulties.

The results have shown that Dennhardt's data are quite untrustworthy (for other evidence, see below), and that oleic acid also, in all concentrations, is a simple electrolyte, only very slightly dissociated. Consequently, the theoretical difficulties of interpretation vanish, and it seems quite possible that a number of other similar cases may also be due to experimental error.

Experimental.

Dry ethyl alcohol was prepared from absolute alcohol which had been kept over specially burnt quicklime for three years; during

* "Colloidal electrolytes are salts in which one ion has been replaced by a heavily hydrated micelle that conducts electricity just as well or even better and carries an equivalent sum total of electrical charges." (See McBain, *Trans. Faraday Soc.*, 1913, **9**, 99. *Kolloid Zeitsch.*, 1913, **13**, 56; T., 1914, **105**, 957, and McBain and Salmon, *J. Amer. Chem. Soc.*, 1918.

this time, the liquid had become a soft, pale yellow jelly owing to the formation of calcium ethoxide. The alcohol was distilled from this material and preserved with the usual precautions. Three separate specimens were used, and identical results obtained in molecular weight determinations. It had D_4^{15} 0·7925, a value only 0·1 per cent. too low, indicating, presumably, the presence of a small amount of ether (water would affect the density in the opposite direction).

All vessels and instruments were carefully calibrated, and the precautions described in earlier papers from this laboratory observed. The oleic acid used was colourless, almost odourless, melting at 9·0°, and having D_4^{18} 0·8938.

Dry potassium oleate was prepared in the following manner. Potassium balls were cleaned by washing with several changes of methylated ether; the balls were at once wiped with filter paper and dropped into dry alcohol. Finally, oleic acid was added to the potassium ethoxide until a sample diluted with about one-quarter of its weight of water (previously boiled) gave a neutral reaction towards phenolphthalein. The solution was then evaporated under diminished pressure over calcium chloride, the potassium oleate being left as a soft, pure white powder.

Molecular Weight of Potassium Oleate in Anhydrous and Moist Alcohol.

Beckmann's ordinary apparatus was employed. Concentrations are expressed in mols. per 1000 grams of alcohol (weight normality).

Concentration.	Grams per 100 grams of alcohol.	Rise in boiling point.	Molecular weight.
0·14	4·518	0·173°	303·4
0·32	10·21	0·388	302·4
0·44	14·09	0·528	306·7
0·49	15·71	0·590	306·1
0·54	17·34	0·654	305·2
0·63	20·16	0·764	303·2
0·70	22·32	0·820	305·6
0·84	26·91	1·008	306·9
0·91	29·18	1·100	305·2
1·00	32·04	1·238	297·9
1·14	36·80	1·350	311·6
		Mean	304·9
		Theory	320·5

The experiments comprise a number of independent series extending up to fully saturated solution. The results show no tendency for the molecular weight to alter with concentration, and they give data rather smaller than that required for the simple molecular weight. This is explained by the moderate dissociation measured below. The value here obtained agrees substantially

with that which Krafft himself found in his second paper, namely, 347, instead of twice the molecular weight.

On the addition of 1, 2, 3, and 4 per cent. of water to the solution, only a very slight alteration in the molecular magnitude was observed, the soap still having a simple molecular weight instead of the larger numbers, namely, 599 to 670, obtained by Krafft and Strutz in their first paper, which appear to be erroneous (see below).

Only the data for the addition of 3·8 per cent. of water (by weight) to the solvent need be presented.

Concentration.	Grams per 100 grams of alcohol.	Rise in boiling point.	Molecular weight.
0·205	6·697	0·243°	311·9
0·278	8·978	0·330	309·7
0·339	10·86	0·400	311·1
0·463	14·84	0·540	315·7
		Mean ...	311·9
		Theory ...	320·5

Krafft considered that his own experiment had confirmed his earlier work with Strutz, for, on the addition of 1·5 c.c. of water to the boiling alcoholic solution, the boiling point was depressed by 0·09°. He appears to have overlooked the fact that a mixture of alcohol and water, containing 96 per cent. of the former, gives a minimum constant-boiling mixture, and therefore the addition of 4 per cent. of water will lower the boiling point of dry alcohol or any solution made from it by about 0·126°. Krafft's experiment, then, if properly calculated, corroborates that just described, and consequently this earlier work is disproved.

Conductivity of Potassium Oleate in Dry Alcohol.

Closed cells of borosilicate glass were employed. The solutions were either made up in the cell by weighing in the constituents or they were made up *ad hoc* and immediately introduced for measurement.

A preliminary experiment on a nearly saturated solution at 18° gave a molecular conductivity of 1·01 mhos. This solution contained 0·1990 gram of potassium oleate in 16·10 grams of alcohol, and therefore its weight-normality was 0·385N, or nearly 0·3N by volume.

The significance of this result depends on the value of the conductivity, at infinite dilution, in alcohol, which is generally accepted as being one-third of the value in aqueous solution. This leads to a value for α, the degree of ionisation, of 3 per cent.

The solubility increases rapidly on heating, and since it is

impossible to predict the behaviour of non-aqueous solutions on further concentration, the remaining measurements were carried out at 40° and 60°. These are given in table I.

TABLE I.

Conductivity of Potassium Oleate in Ethyl Alcohol at 60°.

Weight normality.	Volume normality.	Density.	Specific conductivity.	Molecular conductivity.
1·14	0·68	0·8220	0·001927	2·806
0·76	0·49	0·8030	0·001812	3·679
0·57	0·38	0·7920	0·001694	4·421
0·46	0·31	0·7850	0·001566	5·045
0·38	0·27	0·7800	0·001452	5·483
0·30	0·22	0·7750	0·001285	5·948
0·23	0·16	0·7705	0·001187	7·053
0·14	0·11	0·7640	0·000891	10·64
0·03	0·02	0·7565	0·000381	19·20
		Conductivity at 40°.		
0·57	0·39	0·8013	0·001477	3·799
0·46	0·32	0·7961	0·001372	4·359
0·38	0·27	0·7922	0·001291	4·800
0·30	0·22	0·7884	0·001734	5·182
0·23	0·17	0·7848	0·001031	6·160
0·14	0·11	0·7810	0·0008143	7·567
0·03	0·026	0·7755	0·0003420	13·43

The determinations of the densities of the concentrated solutions were not easy, since the solutions frothed readily and on slight cooling solidified in the form of a curd. For these, the arms of the pyknometer were made vertical, with the mark on one just opposite the tip of the other. Around the latter a glass mantle was fitted by means of a loose cork, and the solution was protected from the cork by a thin layer of clean mercury. During the adjustment, this reservoir was raised, so that the open tip of the pyknometer was immersed in the soap solution. As soon as the adjustment to the mark had been made, the reservoir was lowered and emptied, leaving the pyknometer exactly full and completely immersed in the thermostat.

The density is nearly, although not quite, proportional to the concentration. In the case of oleic acid, the divergence from a straight line is slightly greater.

It is seen from the above tables that the conductivity at 60° rises steadily from 2·81 mhos for a 1·14N(weight)-solution up to the fairly large value of 19·2 for a 0·03N(weight)-solution, without exhibiting any irregularities.

Since the conductivity at infinite dilution at 60° probably lies between 50 and 60 mhos., the dissociation evidently rises from a value of about 3 per cent. in N-solution to about 30 per cent. in

0·03*N*-solution. In every case, then, practically all the soap is in crystalloidal form, although, no doubt, a very small amount of colloid must be present.

Oleic Acid in Dry Alcohol.

Oleic acid is a typical case of a substance giving anomalous data in non-aqueous solution, consequently its molecular weight by the ebullioscopic method was first studied.

The results of several series of determinations may be summarised as follows.

From 0·2898 gram to 6·914 grams of acid were dissolved in 12·96 grams to 13·33 grams of alcohol, giving solutions which were 0·07, 0·08, 0·1, 0·26, 0·3, 0·56, 0·60, 0·80, 0·97, and 1·8*N*(weight), and from the rise in boiling point the following molecular weights are calculated: 297·2, 283·1, 273·6, 270·5, 284·0, 276·0, 294·2, 298·5, 288·1, and 306·9. Mean, 287·1; Calc., 282·3. Difference, 1·7 per cent. There is therefore no doubt with regard to the simple value for the molecular weight or to its constancy over this very great range of concentration. There is clearly also very little dissociation.

We possess very little or no information with regard to the molecular weight of higher fatty acids in water on account of their insolubility in this medium. In quinoline, however, Gabel (*Diss.*, Magdeburg, 1906) found that stearic acid had simple molecular weight, although sodium stearate and palmitate were shown to be colloids.

The next step was to redetermine the conductivity of oleic acid in alcohol. This was measured only at 60°, and the results are given in table II. Every point was determined several times with

TABLE II.

Conductivity of Oleic Acid in Dry Alcohol at 60°.

Weight normality.	Volume normality.	Density.	Specific conductivity.	Molecular conductivity.	$\mu/\sqrt{v}\times 10^{-4}$.	$\mu/\sqrt{v}\times 10^{-4}$. corrected[1]
3·64	1·536	0·8368	$1·57\times10^{-6}$	$3·58\times10^{-3}$	0·24	0·16
1·81	0·955	0·7961	4·01 ,,	4·20 ,,	1·30	1·14
1·44	0·811	0·7905	5·40 ,,	6·66 ,,	1·90	1·72
0·91	0·564	0·7794	5·52 ,,	9·77 ,,	2·30	2·11
0·75	0·482	0·7761	6·56 ,,	13·59 ,,	3·00	2·76
0·47	0·319	0·7695	5·60 ,,	17·54 ,,	3·13	2·85
0·39	0·268	0·7677	5·21 ,,	19·43 ,,	3·20	2·88
0·33	0·238	0·7656	5·04 ,,	21·65 ,,	3·20	2·90
0·13	0·095	0·7593	4·17 ,,	43·85 ,,	4·30	3·76
0·06	0·044	0·7568	2·42 ,,	55·08 ,,	3·60	2·90
0·115	0·011	0·7542	1·21 ,,	110·8 ,,	3·70	2·15
0·011	0·008	0·7540	1·21 ,,	138·2 ,,	4·08	2·40

independent solutions. Some measurements with intermediate concentrations are omitted, to save space, but they fit in smoothly with those presented here.

It will be noticed that the conductivity is very low, making accurate measurement difficult. It is, however, sufficiently higher than that of alcohol itself ($4{\cdot}9 \times 10^{-7}$ at 60°) to make it unmistakable.

In the second place, in contrast to Dennhardt's data (*loc. cit.*), the conductivity rises steadily on dilution. Dennhardt's measurements appear to be inaccurate, and it may be pointed out that Kahlenberg and Schreiner (*Zeitsch. physikal. Chem.*, 1898, **27**, 552) obtained conductivity data for aqueous solutions of sodium oleate which are twice as great as those determined by Dennhardt. In quoting the latter, Goldschmidt remarks (Ubbelohde and Goldschmidt, "Handbuch der Oele und Fette," 1911, III, 47) that the experimental results appear to be due to some error. Again, Dennhardt's data for aqueous potassium oleate differ in some cases from those of Kurzmann (*Koll. Chem. Beihefte*, 1914, **5**, 427) by as much as 30 mhos.

It is very satisfactory to find that the complicated relationships observed by Dennhardt have no real existence, for it would be difficult to explain them, although other similar cases are to be found in the literature of non-aqueous solutions. The point is that they appeared to occur in a substance of simple molecular weight and in regions of extremely low concentration of ions. Thus a mere trace of ion would have to possess a quite impossibly great intrinsic dissociating power, enormously greater even than the sufficiently improbable value ascribed to ionised potassium chloride by Walden (dielectric constant calculated as 14,000). The other alternative would have to be that the ions possessed great tendency towards complex-formation, even in extreme dilution, without, however, an appreciable proportion of the corresponding undissociated complex being formed, even in very concentrated solutions.

Godlewski (*Bull. Acad. Sci. Cracow*, 1904, **6**, 239) found that eight organic acids exhibited in alcohol conductivities of the same order of magnitude as that described above for oleic acid. Further, these acids obeyed the law of mass action. When the ionisation is so small, the law of mass action requires that $\mu/\sqrt{v}$ should be a constant, where μ is the molecular conductivity and v the dilution in litres.

In table II, the penultimate column contains the values of this expression $\mu/\sqrt{v}$, and the last column the same expression corrected for the conductivity of the alcohol. In both cases it is quite

definitely shown that the values are not constant for solutions of greater concentration than $N/8$ or $N/2$ respectively, but both expressions are appreciably constant for the more dilute solutions. The uncorrected values must ultimately continue to rise almost in proportion to the dilution, owing to the fact that the specific conductivity is to be very largely ascribed to the alcohol.

The corrected values are constant, for the fifty-fold range of dilution below $N/2$, within the experimental error, which is, however, necessarily rather large. In other words, the law of mass action applies to these results. The conductivity of the highest concentrations diminishes rapidly, obviously because the solvent is being altered from alcohol to a mixture in which oleic acid actually preponderates.

Wightman, Lloyd, Wiesel, and Jones (*J. Amer. Chem. Soc.*, 1914, **86**, 2243; 1916, **88**, 121) have measured the conductivity of more than forty organic acids in alcohol, including a few of those measured by Godlewski, and find a conductivity of the same magnitude, but the conductivity does not obey the law of mass. Their results, like Wilderman's (*Zeitsch. physikal. Chem.*, 1894, **14**, 231, 247), tend to increase almost as fast as the dilution, instead of being proportional to the square root of the dilution. This deviation from the law of mass action is consequently in the opposite direction from that observed for strong electrolytes in aqueous solution.

It appears possible that Jones's data were not corrected for the conductivity of the alcohol, although in $N/512$-solution this amounted to more than two-thirds of the conductivity. Their results in some cases obey the law of mass action if corrected, some are erratic, a few diminish rapidly, whilst half still rise with dilution.

It is really not surprising that the law of mass action is not always observed, as the relationships are complicated by the esterification which slowly takes place. This must remove hydroxyl ions formed by the alcohol and enhance the amount of ethyl ions present.

The slow esterification does not alter the conductivity much, in spite of the water formed. A $3{\cdot}4N$(weight)-solution does not alter in conductivity at 60° by more than 1 or 2 per cent. in six hours from the time of preparation. According to Jones and his coworkers, a certain amount of esterification must occur, although they found the rate to be independent of the temperature within their experimental error. Dennhardt (*loc. cit.*) found in an 18·4 per cent. solution of oleic acid in methyl alcohol an increase of only 2·9 per cent. in fifteen hours at 25°, and an increase of

4 per cent. in a 36 per cent. solution in fifteen hours. In an 18·5 per cent. solution in ethyl alcohol he observed an increase of 0·2 per cent., and in a 53 per cent. solution an increase of 2·6 per cent. in specific conductivity.

Although in a given time the proportion of acid converted into ester and water would be about the same for any one temperature, independent of the concentration; on diluting there is now more than one substance present, of which the dissociation, and therefore the conductivity, is increasing with dilution. This would seem to explain the general nature of the results, but a study of the esters in alcoholic solution and further knowledge of the part the ions play in the mechanism of the reaction are required for a full discussion of the phenomena.

No stress can be laid on the confirmation of the law of mass action by some acids in alcoholic solution, since all such systems are either in process of reaction or have attained equilibrium through the presence of a large amount of ester.

Mixtures of Oleic Acid and Potassium Oleate in Alcohol.

There is a slight but distinct tendency for oleic acid and potassium oleate to unite, with the formation of a complex. This is shown by the following ebullioscopic data for mixed solutions, where the concentration of the oleate was $0{\cdot}16N$(weight) and that of the oleic acid varied from $0{\cdot}27N$ to $0{\cdot}57N$. The molecular weights found were 311·9, 289·1, 296·4, 322·8. Mean, 305·0; Calc., 282·3. Difference, 7·4 per cent. Found above (p. 440), for pure oleic acid solutions, 287·1.

The conductivity of potassium oleate in alcohol is diminished by the addition of oleic acid to the solution. For instance, $0{\cdot}28N$(weight)-solution of potassium oleate at 60° possessed a specific conductivity of 0·001552; on adding 2·88 equivalents of oleic acid [$2{\cdot}88 \times 0{\cdot}28N$(weight)], the specific conductivity was lowered by 44·3 per cent. to 0·000865. A $0{\cdot}34N$(weight)-solution of the oleate exhibiting a conductivity of 0·001381 on addition of 0·164 equivalent ($0{\cdot}164 \times 0{\cdot}34N$) of oleic acid gave the value 0·001336, a lowering of 3·3 per cent. Although the lowering is thus proportional to the oleic acid added, the effect is not simply dilution of the solution by indifferent oleic acid, since in the first case the weight of oleic acid was only 21 per cent. of the total weight of solution. This shows again that a certain amount of a complex is formed.

Summary.

In moist as well as in dry alcohol, potassium oleate is a typical simple electrolyte moderately dissociated. Oleic acid, contrary to previous data, is also a normal electrolyte exceedingly little dissociated, but apparently obeying the law of mass action on dilution. In mixtures of oleic acid with potassium oleate, a small amount of a complex compound is formed, which tends to show that a small proportion of the ions of the oleic acid itself are also complex. This trace probably accounts for the slight but distinct tendency of all these solutions towards opalescence and frothing.

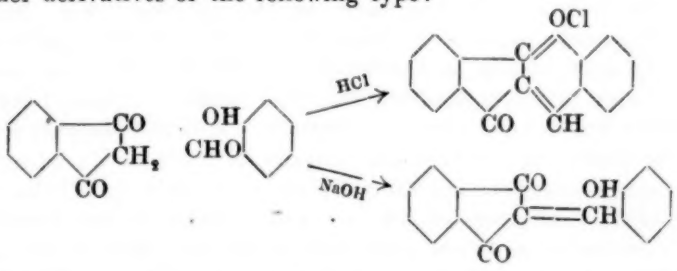
My thanks are due to Dr. J. W. McBain, at whose suggestion this work was carried out, and also to the University Colston Society for a grant which has defrayed the expenses of this investigation.

CHEMICAL DEPARTMENT,
BRISTOL UNIVERSITY. [*Received, March 14th*, 1918.]

XXXVII.—*Synthesis of Pyranol Derivatives.*

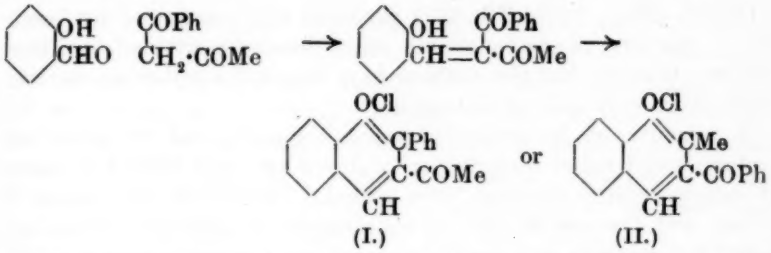
By SARAT CHANDRA CHATTERJI and BROJENDRA NATH GHOSH.

IT has been shown by one of us (T., 1915, **107**, 1442) that diketohydrindene condenses with *o*-hydroxyaldehydes, giving ketoindopyranol derivatives of the following type:



It is apparent that the existence of the ·CO·CH$_2$·CO· group in diketohydrindene is responsible for these changes, and in order to show that the reaction is a general one, we have extended the investigation to other substances containing this group. In the present paper, we describe experiments with benzoylacetone and acetylacetone. One would expect that in these cases also the

interaction between, say, benzoylacetone and salicylaldehyde would proceed in the normal way, yielding condensation products of the following type:



(I.) (II.)

The reaction is not, however, so simple as that indicated by the above equations. Under different conditions, we have been able to isolate three different products from the condensation of these two substances. Two are actually the same as I and II, one being soluble in alcohol and the other insoluble. The former loses hydrogen chloride very readily on exposure to air, and is converted into its base. From its similarity to acetylacetone, we are of opinion that it may have the constitution indicated by I, the insoluble substance having the constitution II. The third product is a complex substance resulting from the reaction of one molecular proportion of salicylaldehyde with two molecular proportions of benzoylacetone, the constitution of which has not yet been determined.

In the case of acetylacetone and salicylaldehyde, two different substances were isolated, one of which was soluble and the other insoluble in acetic acid. In this reaction, the intermediate unsaturated ketone could not be isolated.

In the case of benzoylacetone and salicylaldehyde, the intermediate *salicylidenebenzoylacetone* was obtained by boiling the insoluble compound, formed by their condensation in the presence of hydrogen chloride, with excess of aqueous potassium hydroxide (50 per cent.). The substance, on being boiled with dilute hydrochloric acid, condenses again to the original anhydrohydrochloride (I or II).

The acetyl or benzoyl groups of these substances are very stable, as they are not eliminated on boiling with dilute hydrochloric acid for a long time or even with sodium hydroxide solution.

The bases corresponding with both I and II have also been isolated, their constitutions being represented by the same formulæ except that chlorine is replaced by hydroxyl.

Experimental.

Preparation of Benzoylacetone.

Claisen (*Ber.*, 1887, **20**, 655) prepared this compound by treating a mixture of acetone and ethyl benzoate with alcohol-free sodium ethoxide, but the authors have found the following method much more easy and advantageous.

A mixture of 30 grams of ethyl benzoate and 15 grams of acetone was treated with 50 c.c. of dry ether, and then 4·6 grams of sodium wire or shavings were added. The whole was cooled in water, and the sodium salt at once began to separate. After an hour, the mixture was gently warmed on a water-bath for a few minutes. The precipitate was collected, washed with ether, and then spread on a porous plate. The dried sodium salt was dissolved in a small quantity of hot water, and the cooled solution quickly acidified with dilute sulphuric or acetic acid. The precipitate was collected and washed, and was found to consist of almost pure benzoylacetone.

Condensation of Benzoylacetone and Salicylaldehyde.

Benzoylacetone (6·4 grams) and salicylaldehyde (2·4 grams) were dissolved in the minimum quantity of methyl alcohol, and a current of dry hydrogen chloride was passed through the solution for two hours. The mixture became hot and assumed a dark red colour, but no solid substance separated. After about five hours, the liquid was poured into dilute hydrochloric acid, when a dark green substance separated. This was collected, washed with dilute hydrochloric acid, and finally recrystallised from alcohol containing dilute hydrochloric acid:

0·1389 gave 0·4125 CO_2 and 0·0667 H_2O. C = 80·9; H = 5·3.

$C_{27}H_{20}O_3,\frac{1}{2}H_2O$ requires C = 80·8; H = 5·3 per cent.

The compound crystallises in dark green needles which melt at about 120°. It dissolves in acetic acid, yielding a green solution exhibiting a slight green fluorescence. On boiling with hydrochloric acid, the substance remains unchanged. It forms a very unstable hydrochloride which evolves hydrogen chloride on being kept in a desiccator.

3-Acetyl-2-phenyl-1 : 4-*benzopyranol Anhydrohydrochloride* (I) or *3-Benzoyl-2-methyl*-1 : 4-*benzopyranol Anhydrohydrochloride* (II).

A mixture of 3·2 grams of benzoylacetone and 2·4 grams of salicylaldehyde was dissolved in excess of methyl alcohol, and the

solution cooled in a freezing mixture. A slow current of dry hydrogen chloride was then passed into it, care being taken that no rise of temperature occurred during the reaction. The solution gradually darkened in colour, and a dark red, crystalline substance separated. The mixture was then poured into dilute hydrochloric acid, and the dark, crystalline substance which was obtained in this way was collected and washed with dilute hydrochloric acid. On attempting to recrystallise it from alcohol, it was found that only a small portion of it (*B*) was soluble in alcohol, whereas the bulk of the precipitate (*A*) was insoluble in practically all the ordinary solvents. The substance *A* was kept in a desiccator over potassium hydroxide and analysed:

0·1793 gave 0·4594 CO_2 and 0·0807 H_2O. C = 69·8; H = 5·0.

0·2646 „ 0·1259 AgCl. Cl = 11·8.

$C_{17}H_{13}O_2Cl,\frac{1}{2}H_2O$ requires C = 69·6; H = 4·8; Cl = 12·1 per cent.

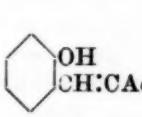
It is a black, crystalline substance which does not melt. It dissolves in concentrated sulphuric acid, forming a red solution which does not show any fluorescence.

The *base* corresponding with the salt (*A*) was prepared by triturating about 1 gram with an excess of a 2 per cent. solution of sodium hydroxide. After keeping the mixture for about half an hour, it was filtered and the residue washed until the filtrate was free from alkali. The substance was then kept in a desiccator over sulphuric acid:

0·1779 gave 0·4679 CO_2 and 0·0916 H_2O. C = 71·7; H = 5·7.

$C_{17}H_{14}O_3,H_2O$ requires C = 71·8; H = 5·6 per cent.

The base is a pale brown substance which is insoluble in all the ordinary solvents. On heating, it does not melt, but chars. It is reconverted into the original salt on being treated with dilute hydrochloric acid.

Salicylidenebenzoylacetone, 

.

This was prepared by heating the insoluble pyranol anhydrohydrochloride with a 50 per cent. solution of potassium hydroxide for several hours. After being cooled, the mixture was acidified with dilute hydrochloric acid, filtered, and the residue washed with hot water. It is a pale brown substance which does not melt on heating, and changes to a chocolate colour on exposure to air:

0·1865 gave 0·5066 CO_2 and 0·0990 H_2O. C = 74·0; H = 5·8.

$C_{17}H_{14}O_3,\frac{1}{2}H_2O$ requires C = 74·1; H = 5·4 per cent.

Attempts to prepare this substance directly by condensing the

constituents in the presence of piperidine or methyl-alcoholic sodium hydroxide were unsuccessful. In every case, a gummy material separated from which no definite substance could be isolated.

Substance B.—As this was formed in very small amount, we isolated it by condensing molecular quantities of benzoylacetone and salicylaldehyde in excess of methyl alcohol and filtering off the precipitate formed. The alcoholic solution was then mixed with dilute hydrochloric acid, when a brown substance separated, which was collected, washed, redissolved in alcohol, and reprecipitated with dilute hydrochloric acid:

0·1815 gave 0·4757 CO_2 and 0·0813 H_2O. C=71·4; H=4·9.

$C_{17}H_{13}O_2Cl$ requires C=71·8; H=4·6 per cent.

This pyranol derivative is a pale brown substance which fuses at a high temperature. On keeping it exposed to the moist atmosphere, it slowly hydrolyses, giving off hydrogen chloride, and being converted into the corresponding base.

The *base* was prepared by dissolving the corresponding anhydrohydrochloride in alcohol and treating the solution with an excess of aqueous sodium acetate. The precipitate was collected, washed with water, and then crystallised from dilute alcohol, when it separated in green prisms, which appeared grey when dry:

0·1426 gave 0·3744 CO_2 and 0·073 H_2O. C=71·6; H=5·7.

$C_{17}H_{14}O_3,H_2O$ requires C=71·8; H=5·6 per cent.

Condensation of Acetylacetone and Salicylaldehyde.

This condensation product was prepared by dissolving 2 grams of acetylacetone and 2·5 grams of salicylaldehyde in the minimum quantity of methyl alcohol, and then saturating the solution with a rapid stream of dry hydrogen chloride for three hours, care being taken to avoid any rise in temperature. The mixture gradually became dark red and soon deposited crystals. The whole was poured into dilute hydrochloric acid, and the substance was collected, washed, and dried. On boiling with acetic acid, it was found that a large portion of it dissolved, but a small quantity remained insoluble although boiled with much acetic acid. The soluble portion was reprecipitated with dilute hydrochloric acid and kept in a vacuum desiccator:

0·2007 gave 0·5617 CO_2 and 0·1009 H_2O. C=76·3; H=5·58.

$C_{17}H_{16}O_3$ requires C=76·1; H=5·9 per cent.

It crystallises in violet-coloured prisms, which do not melt but carbonise on heating. It forms a hydrochloride which, on keeping, gradually loses hydrogen chloride and becomes quite free from

the acid after two or three days. It is soluble in pyridine and other solvents of high boiling point.

The *phenylhydrazone* of this substance was prepared by dissolving 1 gram in glacial acetic acid and boiling the solution with an excess of phenylhydrazine for about half an hour. The mixture, after being cooled, was poured into dilute acetic acid, and the precipitate collected, washed, and recrystallised from alcohol, separating in rose-red needles which melt at a high temperature—above 300°:

0·1431 gave 10 c.c. N_2 at 29° and 756 mm. N = 7·9.
$C_{23}H_{22}O_2N_2$ requires N = 7·8 per cent.

The portion insoluble in acetic acid was kept in a vacuum desiccator over sulphuric acid for several days and then analysed. It was a chocolate-coloured substance which did not melt:

0·1251 gave 0·3383 CO_2 and 0·0605 H_2O. C = 73·7; H = 5·3.
$C_{24}H_{22}O_5$ requires C = 73·8; H = 5·6 per cent.

Our thanks are due to Principal F. W. Südmersen for the kind interest he has taken in the work, and also to the Research Fund Committee for grants which have defrayed the cost of some of the materials used in the work.

CHEMICAL LABORATORY, COTTON COLLEGE,
GAUHATI, ASSAM. [*Received, December 17th*, 1917.]

XXXVIII.—*The Abnormality of Strong Electrolytes. Part I. Electrical Conductivity of Aqueous Salt Solutions.*

By JNANENDRA CHANDRA GHOSH.

VAN'T HOFF discovered that aqueous solutions of electrolytes show an abnormal osmotic pressure. For such solutions, as is well known, the equation $PV = iRT$ holds good. Arrhenius suggested that $i = (1-a) + na$, where a is the degree of dissociation and n the number of ions into which a molecule dissociates. According to Arrhenius, there is, therefore, an equilibrium between ions and undissociated molecules in solution. Ostwald attempted to apply the law of mass action to this case of chemical equilibrium, but his dilution law, $\frac{a^2}{(1-a)V} = K$ fails absolutely in the case of strong

electrolytes. Various hypotheses have been put forward to explain this anomaly, for example, hydration of ions, change in ionic friction with dilution, formation of complexes, action of salts, change in the dielectric constant of the solvent, interaction between molecules and ions, etc. None, however, has been found to be satisfactory. It appears to the present author that the fundamental suggestion of Arrhenius, postulating the co-existence of undissociated molecules and ions in solution, is probably not valid. The question of chemical equilibrium does not enter into the question at all in the case of strong electrolytes. In solutions of strong electrolytes only ions are present, and the attractive forces between ions are only governed by the physical laws of electrostatic attraction. On the basis of this simple assumption, a quantitative interpretation of the increase of molecular conductivity with dilution will be given.

Number of Free Ions in a Solution containing a Gram-molecule of Salt from the Classical Kinetic Theory.—According to a well-known theorem of the kinetic theory of gases, there is a simple relation between the total number of molecules and the number which can perform the work required to displace a molecule from the sphere of mutual attraction. In applying this theorem to calculate the number of free ions in a solution containing a gram-molecule of salt, we may proceed thus:—A salt solution, where only ions are present, is perfectly analogous to a gaseous system. The electrical attraction between the oppositely charged ions corresponds with the molecular forces in an imperfect gas. Due to this attraction, a field of force exists in the interior of a salt solution, the potential of which may be represented by A, that is, A is the work done when the ions constituting a gram-molecule go beyond one another's sphere of attraction. The ions in a solution are, of course, endowed with a kinetic energy of translation, the distribution of velocities being governed by Maxwell's law. As the work done in escaping from the electrical field inside the solution must be derived from the kinetic energy of the ions, only those ions can escape which have a kinetic energy greater than the work to be done. The problem before us is, therefore, to determine what fraction of the total number of ions has a velocity greater than the critical velocity v_0, where $\frac{1}{2}mv_0^2=\frac{A}{nN}$. Here N is Avogadro's number ($6{\cdot}16\times10^{23}$ Millikan's value), n the number of ions into which a molecule dissociates, and $\frac{A}{nN}$ is therefore the work to be done by each ion before it can escape. Now if V' is the most probable speed of an ion, then the fraction we are considering is

represented by $e^{-v_0^2/V^2}$ where e is the base of natural logarithm. Now if c is the square root of the mean of the squares of the speeds, we have $c^2=\frac{3}{2}V^2$, and the required fraction becomes

$$e^{-\frac{1}{3}v_0^2/\frac{1}{3}c^2} = e^{-\frac{1}{2}n.N.mv_0^2/\frac{1}{2}nN.mc^2} = e^{-\frac{A}{nRT}}.$$

(Since there are ions of different equivalent weights in the solution, m signifies the mean mass of an ion.)

As nN is the total number of ions, the number of free ions

$$= nNe^{-\frac{A}{nRT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Conductivity of Salt Solutions.—It is well known that Ohm's law holds good for electrolytic conduction. No energy is therefore lost in overcoming the forces of mutual attraction between ions. Any hypothesis put forward to explain the phenomenon of electrolytic conduction must take into consideration this fundamental fact. According to Arrhenius, the molecular conductivity of a salt solution at infinite dilution is at a maximum, because there the salt is entirely dissociated into ions. With diminishing dilution the molecular conductivity diminishes, because the salt is only partly dissociated and hence the number of ions is less. On the hypothesis that in aqueous solutions we have only ions present subject to forces of electrical attraction, a neat explanation can also be given. Since during electrolytic conduction no energy is lost in overcoming the forces of electrical attraction, only those ions take part in the conduction of electricity which by virtue of their kinetic energy can overcome the forces of mutual attraction. These are also the ions which can be liberated on the electrode surface. The rest are inactive so far as electrical conduction is concerned. At any dilution, the number of free conducting ions is equal to

$$n.N.e^{-\frac{A}{nRT}}$$

where A is the work at that dilution. The molecular conductivity is proportional to this number. At infinite dilution A is zero, since the ions are outside one another's sphere of attraction, and therefore the number of conducting ions is nN. Therefore

$$\frac{\mu_v}{\mu_\infty} = \frac{nNe^{-\frac{A}{nRT}}}{nN} = e^{-\frac{A}{nRT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$A = nRT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad (2')$$

The Electrical Work Necessary to Separate the Component Ions of a Gram-molecule at Various Dilutions.

(a) *The Arrangement of Ions in Solution.*—In the interior of a solution, the electrical forces between ions are balanced. In order that this equilibrium condition may be attained, the ions should arrange themselves in a definite fashion. It is necessary that they should adopt a geometrical disposition of perfect regularity, as do the atoms when they assume a crystalline structure, under the forces of mutual attraction. This does not necessarily mean that the ions in solution are devoid of any kinetic energy whatsoever. What we assume here is that the mean disposition of the oppositely charged ions should conform to some patterns in space. According to Ostwald, the conditions of the salt molecule in the crystalline state is not far removed from the state of solution. Indeed, there is not much difference between a crystalline salt and the same in a molten condition as regards their electrochemical properties. Thus, the experiments of Graetz (*Ann. Phys. Chem.*, 1890, [iii], **40**, 18) have shown that there is no sudden change in electrical conductivity as we pass from the solid to the fused state.

It may well be that even the forces which group the atoms of a solid salt according to a definite space-lattice are electrical in nature. In the first place, therefore, we make the perfectly reasonable assumption that the marshalling of the ions of a salt in a state of solution is analogous to the arrangement of its atoms in the crystalline structure.

(b) *The Forces of Electrical Attraction between Ions.*—For the calculation of the electrical work it is necessary to make another assumption. In solution, an ion takes up a definite mean position because of the forces of electrical attraction exerted by oppositely charged ions surrounding it.

We may, however, suppose that the component ions of a salt-molecule form a completely saturated electrical doublet. When a univalent ion tends to pass out of solution, the solution becomes electrified with an opposite unit charge and attracts it as a whole. By assuming the existence of electrical doublets we only locate the centre of attraction inside the solution. The work necessary for separating the component ions of a molecule is the electrical work done in moving the ions constituting a doublet from their fixed mean distance in the solution to an infinite distance apart. Thus for an aqueous solution of a binary salt like potassium

chloride, the electrical work necessary for separating the potassium and chlorine ions

$$= \frac{E^2}{Dr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where E is the charge on each ion, D the dielectric constant of water, and r the distance between the oppositely charged ions at that dilution.

For salts of the type of barium chloride, there are two electrical doublets associated with each molecule, Cl–Ba–Cl. Now let us remove the two chlorine ions successively from the sphere of influence of the barium ion. For the first chlorine ion, the electrical work is $\frac{E^2}{D.r}$, the same as is necessary for separating the components of a doublet in potassium chloride solutions. The removal of the second chlorine ion is much more difficult. This ion is attracted by two opposite charges, and hence the work due to electrical attraction is $\frac{2E^2}{D.r}$. The work necessary for separating the component ions of a molecule of barium chloride is therefore

$$\frac{3E^2}{D.r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For salts of the type of magnesium sulphate the electrical work is

$$\frac{4E^2}{D.r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

for each ion here carries two unit charges. Now, if we can determine the value of r for these types of salt at various dilutions, A is known, and therefore the ratio $\frac{\mu_v}{\mu_\infty}$, which is equal to $e^{-\frac{A}{nRT}}$ can at once be calculated.

(c) *Calculation of the Distance between Ions in Solutions of Binary Salts.*—The distance between the oppositely charged ions in an aqueous solution can be very simply determined on the assumption previously made. Take, for example, the case of potassium chloride. Bragg has actually measured the distance between the planes 100, 110, 111 of this cubic crystal, and has found that it is the simple cubic lattice to which the arrangement of the atoms conforms. We therefore expect that in solutions, also, the sets of points corresponding with the mean position of the ions form a cubic space-lattice. It is obvious that in a cubic lattice there is only one point, that is, one ion, associated with a unit cell, the distance between the oppositely charged ions being

the linear dimension of the unit cell. Since there are $2N$-ions, the total volume occupied by $2N$-unit cubes $= 2N \cdot r^3 = V$ (c.c. containing a gram-molecule), therefore

$$r = \sqrt[3]{\frac{V}{2N}} \text{ and } A = \frac{N \cdot E^2 \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} \quad . \quad . \quad (6)$$

$$= 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $E = 4{\cdot}7 \times 10^{-10}$[E.S.U.] and $D = 81$ at 18°.

For salts like ammonium chloride or potassium nitrate, where complex univalent radicles are encountered, we are also justified in assuming that the distance between ions at equivalent dilutions is approximately the same as in the case of potassium chloride solutions.

(d) *Calculation of the Distance between Ions in Solutions of Salts like Barium Chloride.*—Crystals of calcium fluoride, the constitution of which is perfectly analogous to that of barium chloride, have been thoroughly investigated by Bragg (*Proc. Roy. Soc.*, 1914, A, **89**, 474). In a fluorspar crystal, the calcium atoms are arranged in a face-centred cube lattice, whilst the fluorine atoms occupy the centres of the small cubes. This structure explains how, for each calcium atom, two fluorine atoms may be arranged to form a cubic lattice. Assuming that the arrangement of the barium and chlorine ions in solution corresponds with the fluorspar lattice, we find that each unit cube of the lattice is associated with half an ion of barium. If r be the linear dimension of the unit cube, since there are N-barium ions, $2N \cdot r^3 = V$ (c.c. containing a gram-molecule), therefore

$$r = \sqrt[3]{\frac{V}{2N}}.$$

The chlorine ions, from analogy, should occupy the centres of unit cubes, hence the distance between the barium ion and the chlorine is $\frac{\sqrt{3}}{2} r$. Therefore the electrical work required to separate the components of a gram-molecule is equal to

$$\frac{3NE^2 \cdot 2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3} \cdot \sqrt[3]{V}} \text{ ergs}$$

$$= 3RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

(e) *Calculation of the Distance between Ions in Solutions of Salts like Magnesium Sulphate.*—No definite structure has yet been assigned to crystals of magnesium sulphate. The fundamental lattice is, of course, not cubic, but a rhombohedron.

It is possible that, owing to the forces of electrical attraction being greater, the oppositely charged ions constituting a doublet should come together as close as possible. Since, however, we are dealing with a salt, the valency volumes of the ions of which are, according to Barlow and Pope's theory, twice as great as that of a univalent ion, the distance between the doublets should be greater than that in the case of potassium chloride. In solution we may take the cube as the fundamental lattice, without introducing any serious error. The above conditions are satisfied if we imagine that the unit cube is formed only by two oppositely charged ions placed at the adjacent corners. The unit cell becomes thus associated with only one-fourth of an ion, as in the cube-centred lattice. If r be the linear dimension of the unit cube at dilution V, then $8N.r^3=V$ (c.c. containing a gram-molecule) or $r=\sqrt[3]{\frac{V}{8N}}$.

r is also the distance between the component ions of a doublet. Therefore the electrical work

$$A=\frac{4.N.E^2\sqrt[3]{8N}}{D\sqrt[3]{V}}=2RT\log_e\frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad (9)$$

From the equations (7), (8), and (9), which contain no unknown quantities whatever, $\frac{\mu_v}{\mu_\infty}$ can be at once calculated for any dilution. In the following tables it will be shown how the observed values of μ_v at 18° agree with those calculated from the above equations. The value of μ_∞ cannot be determined experimentally, but is generally obtained by extrapolation. In the tables, the value of μ_∞ has been calculated from the observed values of μ_v for 0·01N-solutions, and this theoretical value of μ_∞ has then been utilised in calculating μ_v at other dilutions. The observed values of μ_v . × μ_v are from the tables of Kohlrausch and co-workers.

TABLE I.

V = Dilution in litres.

Salt.	μ_∞ calc. from μ_{100}		v = 10.	20.	100.	1000.	5000.
KCl	132·2	μ_v calc.	111·7	115·7	122·5	127·7	129·2
		μ_v obs.	112·0	115·9	122·5	127·6	129·1
NaCl	110·3	μ_v calc.	93·1	96·5	102·0	106·4	108·0
		μ_v obs.	92·0	95·7	102·0	106·5	107·8
LiCl	99·6	μ_v calc.	84·0	87·1	92·1	96·2	97·5
		μ_v obs.	82·4	86·1	92·1	96·5	97·8
CsCl	135·4	μ_v calc.	114·3	—	125·2	130·6	132·5
		μ_v obs.	113·6	—	125·2	130·6	132·0

TABLE I.—(*continued*).

V = Dilution in litres.

Salt.	μ_∞ calc. from μ_{100}		$v = 10.$	20.	100.	1000.	5000.
NH_4Cl ...	132·0	μ_v calc.	111·3	115·4	122·1	127·4	129·3
		μ_v obs.	110·7	115·2	122·1	127·3	128·8
KBr	134·5	μ_v calc.	113·6	117·7	124·4	129·7	131·7
		μ_v obs.	114·2	117·8	124·4	129·4	130·9
KI	133·5	μ_v calc.	112·7	116·7	123·4	128·7	130·6
		μ_v obs.	113·9	117·2	123·4	128·2	129·5
KNO_3 ...	127·9	μ_v calc.	107·8	111·2	118·1	123·3	124·8
		μ_v obs.	105·0	110·0	118·1	122·9	124·3
$NaNO_3$ ...	105·0	μ_v calc.	88·5	91·8	97·1	101·3	102·8
		μ_v obs.	87·4	91·4	97·1	101·8	103·3
$C_2H_3O_2K$	101·6	μ_v calc.	85·9	88·9	94·0	98·1	99·6
		μ_v obs.	84·0	87·7	94·0	98·3	99·6

The agreement is remarkably good. The difference between the observed and the calculated values is rarely greater than 1 per cent.

TABLE II.

V = Equivalent dilution in litres.

μ_v and μ_∞ are equivalent conductivities.

Salt.	μ_∞ calc. from μ_{100}		$v = 10.$	20.	100.	1000.	5000.
$BaCl_2$	124·3	μ_v calc.	92·0	97·3	107·7	116·2	119·5
		μ_v obs.	92·2	96·8	107·7	116·9	119·8
$Sr·Cl_2$	121·6	μ_v calc.	89·3	95·2	105·4	113·8	116·9
		μ_v obs.	90·2	94·4	105·4	114·5	117·5
$CaCl_2$	119·1	μ_v calc.	87·5	93·2	103·2	111·4	114·6
		μ_v obs.	87·9	92·8	103·2	111·5	114·4

The difference between the theoretical and the observed values is never greater than 1 per cent.

TABLE III.

V = Equivalent dilution in litres.

μ_v is equivalent conductivity.

Salt.	μ_∞ calc. from μ_{100}		$v = 10.$	20.	100.	1000.
$MgSO_4$	114·7	μ_v calc.	48·1	57·6	76·6	95·1
		μ_v obs.	50·1	57·0	76·6	100·2
$ZnSO_4$	110·0	μ_v calc.	46·0	55·1	73·4	91·0
		μ_v obs.	46·2	53·5	73·4	98·0
$CuSO_4$	108·0	μ_v calc.	45·2	53·0	72·2	89·6
		μ_v obs.	45·0	51·4	72·2	101·6

At $V=100$ the discrepancy is very large. Below $V=100$ the agreement is quite good. At high dilutions the conductivity is much greater than the calculated value, because of the undoubted hydrolysis of the salts—the interaction between ions and water molecules.

The Temperature-coefficient of the Ratio $\frac{\mu_v}{\mu_\infty}$.—We have seen how the observed values of μ_v agree with those calculated from the equations (7), (8), and (9). There is every reason to believe that the laws of electrical attraction are independent of temperature. The equations, which yield very satisfactory results at 18°, should also hold good at higher temperatures. In our equation for binary electrolytes,

$$A = \frac{N.E^2.\sqrt[3]{2N}}{D.\sqrt[3]{V}} = 2RT\log_e\frac{\mu_\infty}{\mu_v}$$

if the variation of the dielectric constant of water with temperature be known, $\frac{\mu_v}{\mu_\infty}$, can be easily calculated for any temperature. According to Drude, the variation of the dielectric constant of water with temperature between 0° and 76° is given by the following formula:

$$D_t = D_{18}\{1-0{\cdot}00436(t-18)+0{\cdot}0000117(t-18)^2\}.$$

Assuming that this formula holds good up to 100°, the dielectric constant of water at 100° = 52·6. Table IV shows how the calculated values of $\frac{\mu_v}{\mu_\infty}$ at various temperatures agree with the observed data of Noyes and Coolidge (*Zeitsch. physikal. Chem.*, 1903, **46**, 323).

TABLE IV.

Salt.	T°.		v = 12·5.	= 100.
KCl.	18°	$\frac{\mu_v}{\mu_\infty}$ calc.	85·4 per cent.	93·0 per cent.
		$\frac{\mu_v}{\mu_\infty}$ obs.	87·0 ,,	94·0 ,,
	100°	$\frac{\mu_v}{\mu_\infty}$ calc.	82·6 ,,	90·9 ,,
		$\frac{\mu_v}{\mu_\infty}$ obs.	82·6 ,,	91·1 ,,

The coincidence is remarkable. The diminution of the ratio $\frac{\mu_v}{\mu_\infty}$ with increase in temperature may thus be quantitatively explained.

In conclusion, reference should be made to one important point, namely, the question of weak electrolytes. They are invariably either acids or bases. The abnormally high conductivity of hydrogen and hydroxyl ions leaves no room for doubt that here there is a chemical interaction between solvent and solute molecules. Ostwald's dissociation constant is probably related in some way to the constant of these specific chemical reactions.

I take this opportunity of offering my best thanks to Mr. J. N. Mukherjee, M.Sc., for many valuable suggestions. My best thanks are also due to Prof. P. C. Rây.

PHYSICO-CHEMICAL LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

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XXXIX.—*Spinacene and some of its Derivatives.*

By A. CHASTON CHAPMAN.

IN a recent communication (T., 1917, **111**, 56) describing the preparation and properties of spinacene and of some of its derivatives, I directed attention to the fact that the formula for the hydrocarbon based on the analysis of the hexahydrochloride (which was the most crystalline and best defined compound I had succeeded in obtaining) was not in good agreement with the results for the determination of the molecular weight by the cryoscopic method. This discrepancy I was unable to explain, and I therefore determined to prepare a further and larger quantity of the hydrocarbon and also of the hydrochloride. I was fortunately able to obtain some more of the shark-liver oil, and proceeded to prepare spinacene from it by the method previously adopted. As in my earlier work, the main fraction boiled within a range of a few degrees and contained only about 0·5 per cent. of oxygen.

As I had reason to believe that metallic sodium was without action on the hydrocarbon, I proceeded to distil it with the addition of some sodium for the purpose of obtaining a product free from oxygen. In my earlier work, only about 50 c.c. of the oil had been distilled in this manner, and then under a pressure of 10 mm. In the present case, a much larger volume of the oil was employed, and owing to the faulty working of the pump, the pressure during distillation remained constant at about 45 mm.,

the bulk of the oil distilling under that pressure at about 290°. It was noticed that during the distillation the liquid in the flask became increasingly dark in colour, and towards the end had become converted into an almost black, tarry mass.

The portion of the oil, which had distilled over between 280° and 295°, was then submitted to fractional distillation (without sodium) at a pressure varying from 35 to 40 mm., and it was found that the boiling point rose gradually from 84° to 298°.

From this result, it is evident that in the presence of sodium and under the conditions above mentioned, spinacene undergoes some decomposition, and that this method cannot consequently be adopted for its purification. I therefore decided to prepare some more of the spinacene by fractional distillation without the use of sodium and at a pressure not exceeding 10 mm. In these circumstances, a large specimen of the hydrocarbon was obtained having the following properties:

Boiling point	260° (corr.)/9 mm.
Specific gravity (15°/15°)	0·8610
Refractive index at 20°.....	1·4956

When examined by the Wijs method, it was found that 100 parts of the hydrocarbon united with 367·9 parts of iodine.

The following molecular weight determinations were made by the cryoscopic method:

I. 0·2262 in 16·83 benzene gave $\Delta^t = -0·167°$. M.W. = 394.
II. 0·2371 in 17·07 benzene gave $\Delta^t = -0·174°$. M.W. = 391.

This number is higher than that given in my previous paper, and in view of the results obtained in the distillation of this larger quantity of hydrocarbon, the discrepancy is readily explained. Although the breaking up of spinacene when distilled over sodium does not appear to take place at all rapidly until a temperature corresponding with a pressure of about 40 to 50 mm. is reached, there can be no doubt that a little decomposition does occur even at lower temperatures, and that the hydrocarbon which I originally used for the molecular weight determinations must have been contaminated with a little of the decomposition products of lower boiling point.

It may be recalled that the average results of five analyses of the hydrocarbon given in my previous paper were as follows:

$$C = 87·75; \quad H = 12·45.$$

The above results therefore agree well with the formula $C_{29}H_{48}$, which requires C = 87·88; H = 12·12 per cent. M.W. = 396.

Taking the previously determined number for the specific refraction, namely, 0·3394, the molecular refraction is 134·4. Employ-

ing Conrady's average numbers for the atomic specific refractions (D-line), $C_{29}H_{48}$ with six ethenoid linkings requires 134·3. Taking the specific dispersive power of spinacene as 0·0114, its molecular dispersion, $(r\gamma - r\alpha)M$, is 4·51. Taking Eisenlohr's numbers for the atomic dispersion for the α- and the γ-hydrogen lines, the calculated number is 4·21.

As the results of the analysis of the hexahydrochloride which I had previously prepared were in fair agreement with the higher formula, $C_{30}H_{50}$, I determined to prepare a larger quantity of this compound and to submit it to a very thorough process of purification. It was prepared as before, by passing dry hydrogen chloride into a well-cooled solution of spinacene in dry ether. The resulting hexahydrochloride was then purified by dissolving it in warm benzene and adding alcohol until the compound commenced to separate, and finally by crystallising from warm benzene alone. Chlorine estimations were made in each crop of crystals, and the process of recrystallisation was repeated until the chlorine percentage, which showed a tendency to increase, became constant. After the third recrystallisation, the substance was analysed, with the following results:

0·2020 gave 0·2814 AgCl. Cl = 34·45.
0·2145 „ 0·2990 AgCl. Cl = 34·49.
$C_{29}H_{48}$,6HCl requires Cl = 34·60 per cent.

In the process of recrystallisation, the melting point also rose, the final preparation becoming pasty at about 120° and melting to a clear liquid at 126°. During this process of recrystallisation, a small quantity of an oily substance containing about 24 per cent. of chlorine was separated from the mother liquors. It will be seen that the above result is in far better agreement with the formula $C_{29}H_{48}$ than with the formula previously suggested, namely, $C_{30}H_{50}$, which requires Cl = 33·86 per cent. A 5 per cent. solution of the hydrochloride in benzene was found to be optically inactive.

When heated for some time with boiling water, in which it appears to be quite insoluble, no decomposition occurred. When heated, however, for some time with a mixture of alcohol and water, the crystals soon became pasty, and the liquid, after filtering, gave a strong reaction for chloride.

In the course of these experiments, a further quantity of the oily hydrochloride soluble in ether was obtained, but there is some doubt as to the definite character of this compound, and a further study renders it very doubtful whether it constitutes a product intermediate between the hydrocarbon and the crystalline hexahydrochloride.